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by Walter A. Reinhardt and Barrett S. Baldwin, Jr.

Ames Research Center

Moffett Field, Calif.

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A MODEL FOR CHEMICALLY REACTING NITROGEN-OXYGEN MIXTURES

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SUMMARY

An air model is presented that is relatively simple yet quantitatively realistic for use in computing chemical nonequilibrium in a flow field. Such a model is applicable to those computational problems associated with high-speed reentry where the effect of the nonequilibrium processes on the primary flow variables would be important, but where the details of these processes would be of secondary interest. The constituents that comprise the system are N_2 , O_2 , N , O , N^+ , O^+ , and e^- . The dissociation-recombination reactions of N_2 , O_2 , and NO as well as the bimolecular exchange reactions are considered. However, the presence of NO is accounted for in an approximate manner to avoid coupling in the atom conservation equations. The model allows for the inclusion of either nonequilibrium or equilibrium vibration while ionization is taken to be in equilibrium. The resulting rate equations are in a form that may be integrated over local values of the flow variables to obtain a system of transcendental equations that can be solved by iteration. Comparisons with experimental nozzle flow results and with other numerical calculations are presented.

INTRODUCTION

Developments in nonequilibrium flow theory over the past 10 years indicate a need for two types of gas models. Air models based on simplifying approximations have been an important source of qualitative information, whereas attempts to describe specific experimental results have led to great complexity in the models considered. This report presents a simplified model for nitrogen-oxygen mixtures that contains only two nonequilibrium variables for the chemical effects and yet is quantitatively realistic over a wide range of flow conditions.

Early treatments of chemical nonequilibrium in the flow of pure diatomic gases utilized the Lighthill-Freeman model (refs. 1 to 3). This method is based on the assumption that in the presence of chemical reaction any concurrent effect of vibrational nonequilibrium will be minor; a "half excited" value of vibrational excitation is used. Variations on the method allow for a more accurate evaluation of the electronic and vibrational excitation in the equilibrium constant and enthalpy (refs. 4 to 6). For nitrogen-oxygen mixtures, it was determined on the basis of available rate constants that reactions involving nitric oxide would play an important role in shock tube flows (ref. 7). A similar reaction model including vibrational nonequilibrium was

incorporated in a machine program for channel flow (refs. 8 and 9). We shall have occasion to use the results of Emanuel and Vincenti (ref. 9) for purposes of comparison in the present paper. An excellent summary of available information on vibrational and chemical reaction rates believed to be of importance in air flows at temperatures up to 8000° K was given by Wray (ref. 10). A pertinent set of calculations on channel flows and external flows by Eschenroeder et al., emphasize the role of the bimolecular exchange reactions involving nitric oxide (ref. 11). The reaction model used was essentially the same as that of the previous papers except the vibrational excitation was taken to be in equilibrium (we shall also use a representative sample of these calculations as a comparison for our model results). The implications of the existing knowledge on nonequilibrium effects in afterbody flows have been discussed (ref. 12) and possibilities for simplifying the reaction model in certain regimes in studies of complicated geometric configurations were considered (ref. 11).

In the foregoing works a mechanism for coupling between vibrational and chemical nonequilibrium postulated by Hammerling, Teare, and Kivel (ref. 13) was suppressed in the belief that it would be unimportant except at higher temperatures. The available analyses of shock tube data supported this view. Subsequently the theory of such coupling was improved by Heims (ref. 14) and Treanor and Marrone (refs. 15 and 16) and used to explain the results of shock tube experiments in an argon-oxygen mixture at temperatures up to $16,500^{\circ}$ K. Additional coupling mechanisms of possible importance suggested by Bauer and Tsang (refs. 17 and 18) include a rotation-vibration coupling effect and a kinetic effect, due to the bimolecular exchange reactions, that would tend to push the vibrational excitation more rapidly toward equilibrium. Two reports (refs. 19 and 20) have been published that contain a discussion of much of the recent work in the nonequilibrium field as well as details on a general machine program that was used in many of the foregoing studies.

Recently evidence has been uncovered to support the view that (at least in expanding flows) the rates of vibrational relaxation are much greater than the values obtained from previous analyses of shock tube data (refs. 21 to 23). In air mixtures there is evidence that the bimolecular exchange reactions may also promote vibrational relaxation (refs. 17, 18, and 22). Consequently, the accuracy of nonequilibrium theory, as it applies to vibrational relaxation, is still subject to doubt pending further experimental and theoretical investigation. Until the remaining uncertainties are resolved, it is considered worthwhile to allow for the possibility of uncoupled vibrational nonequilibrium. In the following analysis it is a simple matter to include this option and this has been done.

NOMENCLATURE¹

- a ratio of total mass of oxygen to the total mass of nitrogen in a sample of the gas mixture (0.3064 for air)
- b ratio of gram molecular weights, M_O/M_N (1.142)

¹cg.s. units are used.

e_{el}	internal energy contribution due to electronic excitation, equation (5)
$\tilde{e}_{el,i}$	electronic internal energy contribution due to species i , equation (6)
e_{vi}	vibrational contribution to internal energy due to species i , equation (18)
f_N, f_O	variables, defined by equations (27) and (28), that are in the rate equations for production of nitrogen and oxygen
$g_{i,j}$	degeneracy of the j th term level for species i
h	specific enthalpy, equation (3)
\hbar	Planck's constant divided by 2π
K_i	equilibrium constant for i th reaction
k	Boltzmann's constant
$k_{f,i}$	forward rate constant of the i th chemical reaction
M_i	gram molecular weight of species i
m_i	atomic weight of species i
p	pressure
p_r	reservoir pressure
$Q_{el,i}$	electronic partition function for species i , $\sum_j g_{ij} \exp\left(\frac{-\epsilon_{ij}}{kT}\right)$
R	gas constant, equation (7)
\mathcal{R}	universal gas constant
T	temperature
T_r	reservoir temperature
w_N, w_O	degrees of dissociation for nitrogen and oxygen, respectively
y_N, y_O	degrees of ionization for nitrogen and oxygen, respectively
Z	compressibility, equation (2)
$\left. \begin{matrix} \beta_{D,N}, \beta_{D,O} \\ \beta_{I,N}, \beta_{I,O} \end{matrix} \right\}$	variables, defined by equations (12) to (15), and contained in the equations for equilibrium amounts of w_{Ne} , w_{Oe} , y_{Ne} , and y_{Oe} , respectively

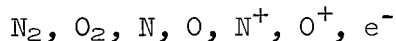
γ_i	specific mole concentration, moles of i per unit mass of gas
δ_i^l	efficiency factor of the l th species for promoting the i th reaction
ϵ_i	measure of the departure of species i from local equilibrium, $w_{ie} - w_i$
ϵ_{ij}	electronic energy corresponding to the j th spectral term for species i
$\left. \begin{matrix} \theta_{R,i}, \theta_{V,i} \\ \theta_{D,i}, \theta_{I,i} \end{matrix} \right\}$	characteristic temperatures for rotation, vibration, dissociation, and ionization, respectively
ρ	density
ρ_0	standard density
τ	characteristic relaxation time
τ_{vi}	characteristic relaxation time for vibration associated with molecular species i , sec

DESCRIPTION OF THE MODEL

In a well-known treatise on the thermodynamic and transport properties of high-temperature air, C. F. Hansen (ref. 24) devised a simplified model for air in equilibrium. The part of this work dealing with thermodynamic properties has fallen into disuse because of the feasibility of tabulating (and including in machine programs) the results of more accurate calculations. In the case of nonequilibrium flows, however, such tabulations are not practical. Consequently, the basic ideas of Hansen are useful in a nonequilibrium model for air and have been applied with slight modifications in the present work.

Equations of State

The species to be included in the expressions representing the equations of state are



At equilibrium any other species that may be present in trace amounts do not affect the equations of state importantly. We assume that this will be true in the nonequilibrium states of main interest also. The omission of NO from the system permits the use of Lighthill variables, that is, degrees of dissociation and ionization. The atom conservation equations are thereby removed from the system of equations to be solved in nonequilibrium problems. Then the equations of state can be written

$$p = R\rho ZT \quad (1)$$

$$Z = \frac{1 + \left[w_N + 2y_N + \frac{a}{b} (w_O + 2y_O) \right]}{1 + \frac{a}{b}} \quad (2)$$

$$h = \frac{7}{2} RT + RT \left(1 + \frac{a}{b} \right)^{-1} \left\{ \frac{1}{2} \left[3w_N + 10y_N + \frac{a}{b} (3w_O + 10y_O) \right] \right. \\ \left. + 2 \left(w_N \frac{\theta_{D,N_2}}{2T} + \frac{a}{b} \frac{w_O \theta_{D,O_2}}{2T} + \frac{y_N \theta_{I,N}}{T} + \frac{a}{b} \frac{y_O \theta_{I,O}}{T} \right) \right\} + e_v + e_{el} \quad (3)$$

where

$$e_{v_{N_2}} = RT \left(1 + \frac{a}{b} \right)^{-1} \frac{1 - w_N}{T} \left[\theta_{v,N_2} \left(\exp \frac{\theta_{v,N_2}}{T} - 1 \right)^{-1} - \theta_{D,N_2} \left(\exp \frac{\theta_{D,N_2}}{T} - 1 \right)^{-1} \right] \quad (4a)$$

$$e_{v_{O_2}} = RT \left(1 + \frac{a}{b} \right)^{-1} \frac{a}{b} \frac{1 - w_O}{T} \left[\theta_{v,O_2} \left(\exp \frac{\theta_{v,O_2}}{T} - 1 \right)^{-1} - \theta_{D,O_2} \left(\exp \frac{\theta_{D,O_2}}{T} - 1 \right)^{-1} \right] \quad (4b)$$

$$e_{el} = RT \left(1 + \frac{a}{b} \right)^{-1} \left((1 - w_N) \tilde{e}_{el,N_2} + \frac{a}{b} (1 - w_O) \tilde{e}_{el,O_2} + 2 \left\{ (w_N - y_N) \tilde{e}_{el,N} \right. \right. \\ \left. \left. + y_N \tilde{e}_{el,N^+} + \frac{a}{b} \left[(w_O - y_O) \tilde{e}_{el,O} + y_O \tilde{e}_{el,O^+} \right] \right\} \right) \quad (5)$$

$$\tilde{e}_{el,i} = \left[\sum_j g_{i,j} \exp \left(\frac{-\epsilon_{ij}}{kT} \right) \right]^{-1} \sum_j g_{i,j} \frac{\epsilon_{ij}}{kT} \exp \left(\frac{-\epsilon_{ij}}{kT} \right) \quad (6)$$

$$R = \frac{\left(1 + \frac{a}{b} \right) R}{2(1 + a)M_N} \quad (7)$$

The term e_v is the vibrational contribution to the energy (per unit mass) and is given by the sum of equations (4a) and (4b) when vibrations are in equilibrium. The description of e_v for nonequilibrium molecular vibration is given subsequently. The parameter a is the ratio of the total mass of oxygen to the total mass of nitrogen in a sample of the gas mixture, and b is the ratio of molecular weights M_O/M_N . The quantities w_N and y_N are the Lighthill variables representing the degrees of dissociation and ionization, respectively, of nitrogen; w_O and y_O are the corresponding variables for oxygen. The relationship between these variables and the species concentrations is given in the appendix. Table I contains the values of the fixed

constants. These expressions correspond to Hansen's model except for the use of truncated harmonic oscillators for the vibrational energies and the addition of a few more terms in the electronic energies of the species. The local equilibrium values of the Lighthill variables can be expressed in the following form that is convenient for calculation.

$$w_{Ne} = y_N + \beta_{D,N} \left[\left(1 + 2 \frac{1 - y_N}{\beta_{D,N}} \right)^{1/2} - 1 \right] \quad (8)$$

$$w_{Oe} = y_O + \beta_{D,O} \left[\left(1 + 2 \frac{1 - y_O}{\beta_{D,O}} \right)^{1/2} - 1 \right] \quad (9)$$

$$y_{Ne} = \frac{1}{2} \left(\beta_{I,N} + \frac{a}{b} y_{Oe} \right) \left\{ \left[1 + \frac{4 w_N \beta_{I,N}}{\left(\beta_{I,N} + \frac{a}{b} y_{Oe} \right)^2} \right]^{1/2} - 1 \right\} \quad (10)$$

$$y_{Oe} = \frac{1}{2} \frac{b}{a} \left(\beta_{I,O} + y_{Ne} \right) \left\{ \left[1 + \frac{4 \frac{a}{b} w_O \beta_{I,O}}{\left(\beta_{I,O} + y_{Ne} \right)^2} \right]^{1/2} - 1 \right\} \quad (11)$$

where

$$\beta_{D,N} = \frac{1+a}{2\rho} m_N \theta_{R,N_2} \left(\frac{m_N k}{2\pi h^2} \right)^{3/2} \frac{Q_{el,N}^2}{Q_{el,N_2}} \sqrt{T} \left[\frac{1 - \exp\left(\frac{-\theta_{v,N_2}}{T}\right)}{1 - \exp\left(\frac{-\theta_{D,O_2}}{T}\right)} \right] \exp\left(\frac{-\theta_{D,N_2}}{T}\right) \quad (12)$$

$$\beta_{D,O} = \frac{b}{a} \frac{1+a}{2\rho} m_N \theta_{R,O_2} \left(\frac{m_O k}{2\pi h^2} \right)^{3/2} \frac{Q_{el,O}^2}{Q_{el,O_2}} \sqrt{T} \left[\frac{1 - \exp\left(\frac{-\theta_{v,O_2}}{T}\right)}{1 - \exp\left(\frac{-\theta_{D,O_2}}{T}\right)} \right] \exp\left(\frac{-\theta_{D,O_2}}{T}\right) \quad (13)$$

$$\beta_{I,N} = \frac{2(1+a)}{\rho} m_N \left(\frac{m_e k T}{2\pi h^2} \right)^{3/2} \frac{Q_{el,N^+}}{Q_{el,N}} \exp\left(\frac{-\theta_{I,N}}{T}\right) \quad (14)$$

$$\beta_{I,O} = \frac{2(1+a)}{\rho} m_N \left(\frac{m_e k T}{2\pi h^2} \right)^{3/2} \frac{Q_{el,O^+}}{Q_{el,O}} \exp\left(\frac{-\theta_{I,O}}{T}\right) \quad (15)$$

and the $Q_{el,j}$ are the electronic partition functions for species j . Again numerical values of the constants are given in table I.

We have compared the values of compressibility Z and specific enthalpy h at equilibrium with those of Hilsenrath and Beckett (ref. 25) and found them to deviate by less than 3 percent at temperatures up to 25,000° K in the density range 0.001-1.0 times atmospheric density.

Ionization has been included in the equations of state so that calculations involving high-temperature equilibrium regions can be made without switching to a different gas model. Ionization nonequilibrium will not be considered. Thus wherever the quantities y_N and y_O appear (eqs. (2) to (5), (8) and (9)), they should be set equal to y_{N_e} and y_{O_e} , respectively (eqs. (10) and (11)). At temperatures below about 10,000° K, y_N and y_O could be set equal to zero.

Rate Equations

Rate equations leading to values of e_v , w_N and w_O appearing in equations (2) and (3) are needed to complete the model. Ionization and electronic excitation are taken to be in equilibrium.

Vibrational nonequilibrium equations.— The rate equations required for uncoupled vibrational nonequilibrium are in a form

$$\frac{de_{vi}}{dt} = -(\tau_{vi})^{-1}e_{vi} + A_{vi} \quad (16)$$

where

$$e_{vi} = e_{vei} - e_{vi} \quad (17a)$$

$$A_{vi} = \frac{de_{vei}}{dt} \quad (17b)$$

The subscript v denotes vibration, subscript e refers to local equilibrium value (eqs. (4a) and (4b)) and the i indicates species (N_2 or O_2). The variable τ_{vi} is a characteristic relaxation time (values of τ_{vi} obtained from ref. 19 are given in table II(b)). The quantity e_v in equation (3) is to be evaluated as

$$e_v = e_{vN_2} + e_{vO_2} \quad (18)$$

rather than $e_v = e_{veO_2} + e_{veN_2}$ as indicated previously for vibrational equilibrium. The quantities e_{vN_2} and e_{vO_2} are obtained from equation (17a); for example,

$$e_{vN_2} = e_{veN_2} - e_{vN_2} \quad (19)$$

Chemical nonequilibrium equations.— The chemical equations of main interest are the dissociation reactions



and the bimolecular exchange reactions



where M denotes any one of the constituents that is catalytic in its effect on a reaction.

The bimolecular exchange reactions (23) and (24) and the NO dissociation-recombination reaction (22) are considered to be the principal mechanisms that establish the balance of nitric oxide in the system. From equilibrium studies it is expected that the nitric oxide will be present in small enough amounts to have negligible effect on the compressibility Z and enthalpy h . However, its presence cannot be ignored since the foregoing reactions taken as a chain can significantly affect the rate of formation of N_2 from N atoms (ref. 11). Since the amount of NO would be relatively constant in such a chain reaction, the steady-state approximation (in which the net rate of production of NO is taken to be zero) will be employed. This approximation leads to an expression for the amount of NO present in terms of the amounts of the more abundant species. That expression can then be used in the rate equations so that the amount of NO no longer appears as a variable.

Upon completion of the foregoing steps and rearrangement, the rate equations can be written

$$\frac{d(w_{Ne} - w_N)}{dt} = - \frac{(w_{Ne} - w_N)f_N}{\tau_{NN}} + \frac{(w_{Oe} - w_O)f_O}{\tau_{NO}} + \frac{dw_{Ne}}{dt} \quad (25)$$

$$\frac{d(w_{Oe} - w_O)}{dt} = \frac{(w_{Ne} - w_N)f_N}{\tau_{ON}} - \frac{(w_{Oe} - w_O)f_O}{\tau_{OO}} + \frac{dw_{Oe}}{dt} \quad (26)$$

Additional details of the derivation are given in the appendix. The quantities f_N , f_O , and τ are given in terms of the state variables by the relations

$$f_N = \frac{(w_{Ne} - 1)(1 - w_N) + (y_N - 1)^2}{(w_{Ne} - y_N)^2} \quad (27)$$

$$f_O = \frac{(w_{Oe} - 1)(1 - w_O) + (y_O - 1)^2}{(w_{Oe} - y_O)^2} \quad (28)$$

$$\frac{1}{\tau_{NN}} = \frac{1}{\tau_N} + \frac{1}{(\tau_{NN})_s} \quad (29)$$

$$\frac{1}{\tau_{OO}} = \frac{1}{\tau_O} + \frac{1}{(\tau_{OO})_s} \quad (30)$$

$$\frac{1}{\tau_{NO}} = \frac{\rho_a}{G} k_{f4} k_{f5} (1 - w_{Ne}) \left(\frac{w_N - y_N}{w_{Ne} - y_N} \right)^2 \quad (31)$$

$$\frac{1}{\tau_{ON}} = \frac{\rho}{G} k_{f4} k_{f5} (1 - w_{Oe}) \left(\frac{w_O - y_O}{w_{Oe} - y_O} \right)^2 \quad (32)$$

$$\frac{1}{\tau_N} = \frac{\rho}{(1+a)M_N} k_{f1} \left\{ \frac{1-w_N}{2} + (w_N - y_N)\delta_1^N + y_N\delta_1^{N+} \right. \\ \left. + \frac{a}{b} \left[\frac{1-w_O}{2} \delta_1^{O_2} + (w_O - y_O)\delta_1^O + y_O\delta_1^{O+} \right] \right\} \quad (33)$$

$$\frac{1}{\tau_O} = \frac{\rho}{(1+a)M_N} k_{f2} \left\{ \frac{1-w_N}{2} \delta_2^{N_2} + (w_N - y_N)\delta_2^N + y_N\delta_2^{N+} \right. \\ \left. + \frac{a}{b} \left[\frac{1-w_O}{2} + (w_O - y_O)\delta_2^O + y_O\delta_2^{O+} \right] \right\} \quad (34)$$

$$\frac{1}{(\tau_{NN})_s} = \frac{\rho \frac{a}{b} k_{f5}}{G} \left\{ k_{f4} (1 - w_{Oe}) \left(\frac{w_O - y_O}{w_{Oe} - y_O} \right)^2 + \left[\frac{k_{f3}\rho}{K_3(1+a)M_N} \right] \left[1 + w_N + \frac{a}{b}(1 + w_O) \right] (w_O - y_O) \right\} \quad (35)$$

$$\frac{1}{(\tau_{OO})_s} = \frac{\rho k_{f4}}{G} \left\{ k_{f5} (1 - w_{Ne}) \left(\frac{w_N - y_N}{w_{Ne} - y_N} \right)^2 + \left[\frac{k_{f3}\rho}{K_3(1+a)M_N} \right] \left[1 + w_N + \frac{a}{b}(1 + w_O) \right] (w_N - y_N) \right\} \quad (36)$$

$$G = (1+a)M_N \left\{ \frac{(1 - w_{Oe})(w_O - y_O)}{(w_{Oe} - y_O)^2} k_{f4} + \frac{(1 - w_{Ne})(w_N - y_N)}{(w_{Ne} - y_N)^2} k_{f5} \right. \\ \left. + \left[\frac{k_{f3}\rho}{K_3(1+a)M_N} \right] \left[1 + w_N + \frac{a}{b}(1 + w_O) \right] \right\} \quad (37)$$

$$K_3 = 3.98 \left(\frac{4500}{T} \right)^{0.15} \exp \left(- \frac{75490}{T} \right) \quad (38)$$

The equilibrium constant, K_3 , was obtained from reference 8. The remaining undefined functions and constants are given in table II. The rate constants utilized here are taken from reference 12.

The quantities τ_N and τ_O are the values of τ_{NN} and τ_{OO} , respectively, that would apply in the absence of the reactions involving NO (i.e., for pure nitrogen or pure oxygen). For those cases, the coupling terms in equations (25) and (26) would be absent. Thus the quantities τ_{NO} , τ_{ON} , $(\tau_{NN})_s$, and $(\tau_{OO})_s$ can be associated with the reactions involving NO, while τ_N and τ_O are due to the nitrogen and oxygen dissociation reactions. It is instructive to observe the behavior of these quantities evaluated under equilibrium conditions.

Figure 1(a) is a plot of the quantity $\rho\tau_{NN}$ at equilibrium as a function of temperature with density as a parameter. The reaction times for dissociation of pure nitrogen τ_N and dissociation of pure oxygen τ_O also appear in

the figure. The products $\rho\tau$ are plotted rather than τ because of the resulting suppression of density dependence. At low temperatures τ_{NN} is approximately equal to τ_0 , but with increasing temperature it begins to exceed τ_0 and eventually approaches τ_N . Thus in the low temperature range the nitric oxide chain reactions accelerate the dissociation (or recombination) of nitrogen in such a manner as to make τ_{NN} more nearly equal to τ_0 than to τ_N . In addition equations (25) and (26) indicate that the NO reactions bring about a direct coupling between the degrees of dissociation of nitrogen and oxygen such that one cannot be in equilibrium unless the other is also. The characteristic time τ_{NO} for the rate of dissociation of nitrogen due to a nonequilibrium condition of the oxygen is plotted in figure 1(b).

Figure 2(a) is a plot of $\rho\tau_{OO}$. It is seen that τ_{OO} does not deviate greatly from the reaction time of pure oxygen τ_0 , particularly at the lower densities. However, equation (26) shows that a nonequilibrium condition of the nitrogen will affect the rate of dissociation of oxygen. The reaction time corresponding to this effect τ_{ON} is plotted in figure 2(b). Note that the values of the reaction times appearing in figures 1 and 2 were evaluated at equilibrium. However, their dependence on the composition is weak and will not deviate greatly in nonequilibrium states. This is not true of the factors f_N and f_O appearing in equations (25) and (26) and evaluated in equations (27) and (28). These quantities are usually of order 1.0 but can become large in some circumstances. For example, equation (27) shows that when the local equilibrium value of the degree of dissociation of nitrogen ($w_{Ne} - y_N$) becomes small, the factor f_N will be large. For this reason, if the degree of dissociation of nitrogen is small, the nitrogen reaction can be nearly in equilibrium while the oxygen reaction is frozen. This is an exception to the foregoing argument to the contrary that was based on the values of τ without consideration of the values of f_N and f_O .

NONEQUILIBRIUM CHANNEL FLOW CALCULATIONS

The relations presented in the previous section are applicable to a wide range of flow problems including steady and unsteady one-, two-, and three-dimensional flows. We shall consider only the quasi-one-dimensional case here. In previous calculations of this type one difficulty that has plagued investigators is the singular perturbation effect that arises in near equilibrium flow. The nature of the difficulty in the case of one-dimensional flow can be clarified by reference, for example, to equation (16). In a numerical integration procedure such as the Runge-Kutta method, the right side of equation (16) would be evaluated numerically several times at each step. In a near equilibrium region the factor $(\tau_{vi})^{-1}$ becomes large and $\epsilon_{vi} = e_{vei} - e_{vi}$ becomes small while the product retains an intermediate value that cannot be neglected. From a numerical viewpoint it is clear that evaluation of the product will entail a small difference when $e_{vei} - e_{vi}$ is small. One observes that the chemical rate equations (eqs. (25) and (26)) contain the same near equilibrium indeterminacy. For a gas system involving many reactions the problem is amplified by the occurrence of many terms of this type which may exhibit improper behavior at different points in the flow field. Various remedies for the difficulty have been found (refs. 26 to 28, 11, 19, and 20).

It is perhaps fair to state that in practice these methods lead to a very small step size in the numerical integration. In contrast, the procedure to be described here leads to accurate integrations that require no smaller step size than is needed for the corresponding equilibrium flow. Furthermore, the same nonequilibrium equations are used in the entire flow field including nonequilibrium, near-equilibrium, and equilibrium regions. Recently three new methods for integrating chemical rate equations have appeared in the literature (refs. 29 to 31). These methods also permit greatly increased step size in near-equilibrium flows. We have developed the required technique for integrating an arbitrary number of equations (ref. 32), including coupled-vibrational nonequilibrium, but the procedure for the general case will not be considered here.

The crux of the method lies in the integration of equations (16), (25), and (26) over a small interval Δt . For example, equation (16) may be integrated exactly to obtain

$$\epsilon_{vi}|_2 = \left[\epsilon_{vi}|_1 + \int_0^{\int_{t_1}^{t_2} \frac{d\eta}{\tau_{vi}}} A_{vi} \tau_{vi} \exp(u) du \right] \exp\left(-\int_{t_1}^{t_2} \frac{d\eta}{\tau_{vi}}\right) \quad (39)$$

The subscripts 1 and 2 define the interval of integration and $\Delta t = t_2 - t_1$. Using mean value integral theorems, we may write equation (39)

$$\epsilon_{vi}|_2 = \epsilon_{vi}|_1 \exp\left[-\frac{\Delta t}{(\tau_{vi})_{\xi_1}}\right] + (A_{vi} \tau_{vi})_{\xi_2} \left\{1 - \exp\left[-\frac{\Delta t}{(\tau_{vi})_{\xi_1}}\right]\right\} \quad (40)$$

The subscripts ξ_1 and ξ_2 denote that τ_{vi} and the product $(A_{vi} \tau_{vi})$ are evaluated at different instants of time in the interval Δt which includes both ξ_1 and ξ_2 . The closed form integration given by equation (40) is exact, but in practice it is difficult to evaluate since the quantities $(\tau_{vi})_{\xi_1}$ and $(A_{vi} \tau_{vi})_{\xi_2}$ are not readily obtained. However, if τ_{vi} and A_{vi} are evaluated at the midpoint of the interval Δt and are monotonic over the interval, it can be shown that the error in ϵ_{vi} is of order

$$\epsilon_{vi}(\Delta t)^3 \exp\left(-\frac{\Delta t}{\tau_{vi}}\right) \quad (41)$$

In nonequilibrium regions of a channel flow calculation the τ_{vi} has small enough values that the exponentials in equation (40) could be expanded to order $(\Delta t)^2$ without loss of accuracy. There would then be no difficulty in a numerical integration of equation (16) or for that matter of equations (25) and (26). For near-equilibrium regions, however, τ_{vi} becomes small, so the expansion is valid only for very small Δt . This is the reason a small step size would be required for numerical integration of equation (16). If the closed form integration is used instead, the error becomes vanishingly small under these conditions because of the exponential factor in the error term above.

The ideas incorporated in the integration of the vibrational rate equation are adaptable to integration of the coupled chemical rate equations given by equations (25) and (26). For that purpose these equations can be written in the form

$$\frac{d\epsilon_1}{dt} = -a_{11}\epsilon_1 + a_{12}\epsilon_2 + A_1 \quad (42)$$

$$\frac{d\epsilon_2}{dt} = a_{21}\epsilon_1 - a_{22}\epsilon_2 + A_2 \quad (43)$$

where

$$\epsilon_1 = w_{Ne} - w_N \quad (44a)$$

$$\epsilon_2 = w_{Oe} - w_O \quad (44b)$$

$$a_{11} = f_N/\tau_{NN} \quad (44c)$$

$$a_{12} = f_O/\tau_{NO} \quad (44d)$$

$$a_{21} = f_N/\tau_{ON} \quad (44e)$$

$$a_{22} = f_O/\tau_{OO} \quad (44f)$$

$$A_1 = dw_{Ne}/dt \quad (44g)$$

$$A_2 = dw_{Oe}/dt \quad (44h)$$

The quantities ϵ_1 and ϵ_2 are chemical nonequilibrium variables similar in character to ϵ_{v1} in that they are measures of the departure from equilibrium. The closed-form solution of these equations is

$$\epsilon_i = B_{i1} \exp(-\lambda_1 \Delta t) + B_{i2} \exp(-\lambda_2 \Delta t) + C_i \quad (i = 1, 2) \quad (45)$$

where

$$\left. \begin{matrix} \lambda_1 \\ \lambda_2 \end{matrix} \right\} = \frac{1}{2} \left\{ (a_{11} + a_{22}) \pm [(a_{11} - a_{22})^2 + 4a_{12}a_{21}]^{1/2} \right\} \quad (46a)$$

$$B_{11} = [(a_{11} - \lambda_2)\epsilon_{p1} - a_{12}\epsilon_{p2}]/(\lambda_1 - \lambda_2) \quad (46b)$$

$$B_{12} = -[(a_{11} - \lambda_1)\epsilon_{p1} - a_{12}\epsilon_{p2}]/(\lambda_1 - \lambda_2) \quad (46c)$$

$$C_1 = (a_{22}A_1 + a_{12}A_2)/(a_{11}a_{22} - a_{12}a_{21}) \quad (46d)$$

$$\epsilon_{p1} = (\epsilon_1)_0 - C_1 \quad (46e)$$

The quantities B_{22} , B_{21} , C_2 , and ϵ_{p2} can be obtained from the above relations by interchanging indices 1 and 2. The quantities $(\epsilon_1)_0$ and $(\epsilon_2)_0$ are the values of ϵ_1 and ϵ_2 at the beginning of the interval Δt . This is not an exact integration since the a_{ij} and A_i are evaluated at the midpoint of the interval Δt in the same manner as suggested in the discussion following the

integration of the vibrational rate equations. The error is of the same order as given by the relation, equation (41).

The remaining equations for quasi-one-dimensional flow can be found in many of the foregoing references (e.g., ref. 8). To save space these will not be repeated here. The closed form integration of the rate equations could be combined with the remaining flow equations in several ways. We have used an iteration procedure. Our program includes options for performing integrations with a specified pressure distribution $p(x)$ or a specified area distribution $A(x)$. In the latter case a procedure is included for iterating to find the mass flow in the presence of nonequilibrium effects ahead of the throat. Integrations from the stagnation region to the throat are then usually repeated three or four times. Provision is made for iterating to find the conditions behind a normal shock, and by setting $A(x)$ equal to a constant, the nonequilibrium flow behind a normal shock can be calculated.

Our program contains options for including or excluding uncoupled vibrational nonequilibrium effects. Any of the rate constants can be separately set equal to a large value to obtain calculations corresponding to partial or complete equilibrium. Also the rate constants can be set equal to zero to obtain frozen flow calculations. In all of these cases the integration method is unchanged and remains the same in all regions of the flow since it is valid in the entire spectrum of equilibrium, nonequilibrium, and frozen flows. The step size is variable to conform with the requirement of a specified permissible deviation of the values of the key variables computed in two different ways (direct calculation and extrapolation from results at previous points). Thus nonanalytic behavior of the specified function $A(x)$ leads to a decrease in step size and is followed faithfully by the calculation. Accurate calculation of a nozzle flow (less than 0.1 percent change from reducing the step size criterion by a factor of 2.0) typically requires less than 200 steps. The average computing time on an IBM 7094 is about 45 seconds per case for equilibrium, nonequilibrium, or frozen-flow calculations.

EVALUATION OF APPROXIMATE MODEL

The major consideration here is to evaluate the use of the steady-state approximation as a means of simply including the effects of the bimolecular exchange reactions. This is perhaps best done by comparison of the results with other numerical calculations and with experiment. For the comparisons with other numerical calculations we have chosen the work of Emanuel and Vincenti (ref. 9) and the work of Eschenroeder, Boyer, and Hall (ref. 11). Complete listings for the latter calculation including temperature, pressure, and composition profiles were kindly provided upon request by Dr. D. W. Boyer of the Cornell Aeronautical Laboratory. The experimental comparisons are based on references 21 to 23, 33, and 34.

Figure 3 includes temperature profile plots of a nozzle calculation obtained from the model and from Emanuel and Vincenti (ref. 9). The small differences indicate: (1) that there are no gross errors in either calculation; and (2) that the steady-state approximation for the nitric oxide chain

reactions is valid for this case. The other flow field variables such as pressure, density, and velocity are less sensitive to the gas model used than is the temperature. No observable differences were noticed between the published curves and the model results for these variables.

The compositions resulting from the two calculations are compared in figure 4. Here the differences are greater because of the omission of nitric oxide from our model. Consequently, the amounts of N_2 , O_2 , N , and O are all larger in our calculation than in that of Vincenti and Emanuel. However, the situation here is similar to that which exists in the comparisons at equilibrium, previously discussed. Namely, replacing NO with varying amounts of the other species in the equations of state has less effect on the enthalpy h and the compressibility Z than might at first be expected. This is borne out by the close agreement between temperature distributions shown in figure 3. The composition profiles may be computed more accurately if a correction discussed in the appendix is used. This was not done here to emphasize the fact that a good comparison is obtainable without accurate values for the concentration variables.

Figure 5 shows four separate plots of temperature versus area ratio. One pair of curves represents a comparison of the model with the results of Eschenroeder, et al. (ref. 11) where the chemistry is in nonequilibrium and the vibrational degrees of freedom are in equilibrium. The other pair of curves is a comparison of calculations assuming complete equilibrium. One observes that the equilibrium calculations are in excellent agreement, as would be expected. The differences are greatest at the lower temperatures (and far downstream of the throat) where the omission of nitric oxide from the equations of state has its largest effect on the enthalpy and compressibility. The differences are greater, however, in the comparisons of the nonequilibrium calculations although the agreement is still excellent at the throat where the flow field is in local equilibrium. Downstream the flow field remains in equilibrium longer for the model than the results of Eschenroeder, Boyer, and Hall indicate. Whether the differences are due to the NO approximation or to the different methods used in integrating the near-equilibrium region of the flow field is difficult to determine. We did compare the nitric oxide concentration obtained from the steady-state approximation with that obtained from a more accurate relation (see appendix) and noted little difference.

In figure 6 results are compared for the corresponding pressure profiles. Although the differences are smaller they still show the same character as discussed above, that is, the comparisons are in good agreement in the equilibrium region of the flow field near the throat. Figure 7 shows a comparison of the composition profiles. Here the concentration variables are corrected by the method described in the appendix. The curves corresponding to the model are labeled γ_{ie} or γ_i depending on whether the variables result from an equilibrium or nonequilibrium calculation. The results of Eschenroeder are indicated by $()_c$. As before, the agreement is excellent near the throat and deviations begin in the near-equilibrium region of the flow field.

Nagamatsu and Sheer have published experimental data on vibrational relaxation and recombination of nitrogen and air in hypersonic nozzle flows (refs. 33 and 34). Their data are given in the form of the ratio of static

pressure to reservoir pressure versus reservoir temperature at various specified reservoir pressures, and at a station in the nozzle where the area ratio (A/A^*) is equal to 144. We have made a series of (about 180) nonequilibrium channel flow calculations for the nozzle shape specified in reference 33. The results are shown in figures 8 and 9 for nitrogen and air, respectively. In each of the figures the circles are the data points of Nagamatsu and Sheer while the four solid curves represent calculations using the model. For brevity the solid line curves are labeled with the numerals (1) through (4), respectively, designating the following types of flow field calculations:

- (1) Complete equilibrium
- (2) Chemical nonequilibrium; vibrational equilibrium
- (3) Chemical and vibration nonequilibrium (for pure nitrogen (figs. 8(a), (b), and (c)), the vibrational rate constants are from ref. 19, while for air (figs. 9(a), (b), and (c)), the vibrational rates are those of ref. 35)
- (4) Frozen (at the reservoir conditions)

The equilibrium and frozen flow calculations are included to establish the trends indicated by the experimental results. Equilibrium flow field calculations correspond to an infinitesimally small relaxation time (infinite rate constant), while frozen calculations correspond to an infinitely large relaxation time (zero rate constant).

The model results for pure nitrogen are given in figures 8(a), (b), and (c) and represent exact calculations since no assumptions are involved (the steady-state approximation does not apply here). One observes that below 5000° K there is a negligible amount of nitrogen molecular dissociation since curves (1) and (2) are coincident. The nonequilibrium effects indicated by (3) and the experimental data are then due primarily to vibrational nonequilibrium. The experimental data points in figures 8(a), (b), and (c) all lie between the curves labeled (2) and (3) indicating that the vibrational rate constants used here are too small. This is in accord with references 21 and 22 where it is suggested that the vibrational rates obtained from shock tube experiments must be greater by a factor of 15 in order to agree with expanding flow measurements.

In figures 9(a), (b), and (c) the experimental results are compared with the model calculations for air. The experimental results are, in general, on or above (3), the curve representing vibrational equilibrium. The trend of these comparisons for air is in accord with references 22 and 23 where it is shown that the chemical equations given by equations (20) to (24) with vibrations in equilibrium (i.e., the model given in ref. 11) provide the mechanism for experimental agreement.

Ames Research Center
National Aeronautics and Space Administration
Moffett Field, Calif., May 5, 1965

APPENDIX

SUPPLEMENTARY EQUATIONS AND DERIVATIONS

Relationship Between Lighthill Variables and Species Concentrations

The species concentrations γ_i (moles of i per unit mass of gas) of the nitrogen components are given by the relations

$$\gamma_{N_2} = \frac{1 - w_N}{2} \gamma_{t,N} \quad (A1)$$

$$\gamma_N = (w_N - y_N) \gamma_{t,N} \quad (A2)$$

$$\gamma_{N^+} = y_N \gamma_{t,N} \quad (A3)$$

Corresponding expressions for γ_{O_2} , γ_O , and γ_{O^+} can be obtained from the above relations by replacing the subscript N with an O . The values of γ_{e^-} and the constants $\gamma_{t,N}$, $\gamma_{t,O}$ are

$$\gamma_{e^-} = \gamma_{N^+} + \gamma_{O^+} = \left(y_N + \frac{a}{b} y_O \right) \gamma_{t,N} \quad (A4)$$

$$\gamma_{t,N} = \frac{1}{(1 + a)M_N} \quad (A5)$$

$$\gamma_{t,O} = \frac{a}{b} \gamma_{t,N} \quad (A6)$$

where M_N is the molecular weight of atomic nitrogen.

Chemical Rate Equations for Dissociation Reactions

The rate equation for reaction 1 (eq. (20)) can be written (see, e.g., ref. 12)

$$\frac{d_1 \gamma_{N_2}}{dt} = - \left(\rho \sum_l k_{F1}^l \gamma_l \right) \left(\gamma_{N_2} - \frac{\rho}{K_1} \gamma_N^2 \right) \quad (A7)$$

The subscript 1 in $d_1 \gamma_{N_2}/dt$ indicates that this is the rate of change of γ_{N_2} due to reaction 1. The index l refers to the catalytic body involved (e.g., N_2 , O_2 , etc.). Upon substitution of equations (A1) and (A2), this becomes

$$\frac{dw_1}{dt} = \left(\rho \sum_l k_{F1}^l \gamma_l \right) \left[1 - w_N - \frac{2\rho}{K_1} \gamma_{t,N} (w_N - y_N)^2 \right] \quad (A8)$$

An expression for the equilibrium constant K_1 in terms of the local equilibrium variables can be found upon noting that the quantity in square brackets is zero at equilibrium; namely,

$$\frac{2\rho}{K_1} \gamma_{t,N} = \frac{1 - w_{Ne}}{(w_{Ne} - y_N)^2} \quad (A9)$$

Substituting this into (A8) and rearranging yields

$$\frac{d_1 w_N}{dt} = \frac{(w_{Ne} - w_N) f_N}{\tau_N} \quad (A10)$$

where f_N and τ_N are given in equations (27) and (33). The corresponding rearrangement of the rate equation for reaction 2 is formally the same, but with the subscript 1 replaced by 2, and the N subscripts replaced by O. The rate constants $k_{f_i}^l$ are given by

$$k_{f_i}^l = k_{f_i} \delta_i^l \quad (A11)$$

where the k_{f_i} and δ_i^l are listed in table II, which is based on reference 12.

Steady-State Approximation

Rate equations corresponding to reactions 3, 4, and 5 can be expressed as

$$\frac{d_3 \gamma_N}{dt} = \frac{d_3 \gamma_O}{dt} = - \frac{d_3 \gamma_{NO}}{dt} = \left(\rho \sum_l k_{f_3}^l \gamma_l \right) \left(\gamma_{NO} - \frac{\rho}{K_3} \gamma_N \gamma_O \right) \quad (A12)$$

$$\frac{-d_4 \gamma_N}{dt} = \frac{d_4 \gamma_O}{dt} = \frac{d_4 \gamma_{NO}}{dt} = \rho k_{f_4} \left(\gamma_{O_2} \gamma_N - \frac{1}{K_4} \gamma_{NO} \gamma_O \right) \quad (A13)$$

$$\frac{d_5 \gamma_N}{dt} = - \frac{d_5 \gamma_O}{dt} = \frac{d_5 \gamma_{NO}}{dt} = \rho k_{f_5} \left(\gamma_{N_2} \gamma_O - \frac{1}{K_5} \gamma_{NO} \gamma_N \right) \quad (A14)$$

The equilibrium constant K_3 is given in equation (38), while K_4 and K_5 can be expressed in terms of K_1 , K_2 , and K_3 by the relations

$$K_4 = \frac{K_2}{K_3} \quad (A15)$$

$$K_5 = \frac{K_1}{K_3} \quad (A16)$$

From the above expressions, the total rate of change of γ_{NO} can be written

$$\begin{aligned} \frac{d\gamma_{NO}}{dt} = & -\rho \left(\sum_l k_{f3}^l \gamma_l + \frac{k_{f4} \gamma_O}{K_4} + \frac{k_{f5} \gamma_N}{K_5} \right) \gamma_{NO} \\ & + \rho \left[\left(\sum_l k_{f3}^l \gamma_l \right) \rho \frac{\gamma_N \gamma_O}{K_3} + k_{f4} \gamma_{O_2} \gamma_N + k_{f5} \gamma_{N_2} \gamma_O \right] \end{aligned} \quad (A17)$$

In the classical steady-state approximation (ref. 36), $d\gamma_{NO}/dt$ is set equal to zero so that a value of γ_{NO} can be obtained from the above relation; namely,

$$\gamma_{NO}^0 = \frac{\left(\sum_l k_{f3}^l \gamma_l \right) \rho \frac{\gamma_N \gamma_O}{K_3} + k_{f4} \gamma_{O_2} \gamma_N + k_{f5} \gamma_{N_2} \gamma_O}{\sum_l k_{f3}^l \gamma_l + \frac{k_{f4} \gamma_O}{K_4} + \frac{k_{f5} \gamma_N}{K_5}} \quad (A18)$$

where the superscript zero denotes that γ_{NO}^0 is a zeroth order approximation for the amount of nitric oxide. This value of γ_{NO}^0 is then substituted in equations (A12) to (A14) to obtain approximate rates of change of γ_N and γ_O due to the reactions involving NO. Upon further substitution of equations (A15), (A16), (A1), (A2), (A9), and the corresponding relations for γ_{O_2} , γ_O , K_2 , and rearrangement, the rate of change of w_N due to the NO reactions can be written

$$\frac{d_3 w_N}{dt} + \frac{d_4 w_N}{dt} + \frac{d_5 w_N}{dt} = \frac{(w_{Ne} - w_N) f_N}{(\tau_{NN})_S} - \frac{(w_{Oe} - w_O) f_O}{\tau_{NO}} \quad (A19)$$

In the derivation of this equation, terms of the type $d_4 w_N/dt$ appear. It can be seen that such terms are zero by noting for example that the foregoing term is proportional to $d_4 \gamma_N/dt$. The latter quantity is clearly zero (i.e., the rate of change of γ_N due to reaction 4 is zero). Expressions for the functions f_N , f_O , $(\tau_{NN})_S$, τ_{NO} are given in the text. Finally, equation (25) is arrived at by adding $d_1 w_N/dt$ to obtain the total rate of change of w_N . The corresponding relations for dw_O/dt can be obtained from the above by interchanging subscripts 4, 5, and N, O.

Correction for Species Concentration Resulting From Nitric Oxide Omission

Equation (A18) yields the nitric oxide concentration resulting from the use of the steady-state approximation. To assess the accuracy of this approximation, γ_{NO}^0 may be compared with γ_{NO}^1 obtained by integrating the nitric oxide rate equation given by equation (A17). This is done by using a method similar to that used to obtain equations (40) and (45). Equation (A17) may be represented by

$$\frac{d\gamma_{NO}}{dt} = -A\gamma_{NO} + B \quad (A20)$$

The variable B includes all the terms in equation (A17) that do not include γ_{NO} and the variable A represents all the terms with γ_{NO} factored out. Equation (A20) is then integrated by the same procedure discussed in the text to obtain

$$\gamma_{\text{NO}}^1 = (\gamma_{\text{NO}}^1)_0 \exp(-A \Delta t) + [1 - \exp(A \Delta t)] \gamma_{\text{NO}}^0 \quad (\text{A21})$$

Here the ratio B/A is replaced by γ_{NO}^0 obtained from the steady-state approximation and $(\gamma_{\text{NO}}^1)_0$ represents the value of γ_{NO}^1 at the beginning of the interval (see paragraph in text preceding eq. (41)).

The values of A and γ_{NO}^0 are obtained by evaluation at the beginning of the interval. The γ_i contained in A and γ_{NO}^0 are corrected in the following manner. The corrections to the number of nitrogen and oxygen atoms, $\gamma_{t,\text{N}}$ and $\gamma_{t,\text{O}}$, are given by

$$\gamma_{t,\text{N}} = \gamma_{t,\text{N}}^1 + \gamma_{\text{NO}}^1 \quad (\text{A22})$$

$$\gamma_{t,\text{O}} = \gamma_{t,\text{O}}^1 + \gamma_{\text{NO}}^1 \quad (\text{A23})$$

where $\gamma_{t,\text{N}}$ and $\gamma_{t,\text{O}}$ are given by equations (A5) and (A6), respectively. Substituting $\gamma_{t,\text{N}}^1$ into equations (A1) to (A3) and $\gamma_{t,\text{O}}^1$ into the corresponding relations for the oxygen species yields the corrected values of the species concentrations.

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TABLE I.- FIXED CONSTANTS REQUIRED FOR NITROGEN AND OXYGEN MIXTURES

i	$\theta_{R,i}, ^\circ K$	$\theta_{V,i}, ^\circ K$	$\theta_{D,i}, ^\circ K$	i	$\theta_{I,i}, ^\circ K$
N ₂	2.86	3340	113260	N	168800
O ₂	2.07	2230	59380	O	158000

j	$\epsilon_{N,j}$	$\frac{\epsilon_{N,j}}{k}$	$\epsilon_{O,j}$	$\frac{\epsilon_{O,j}}{k}$	$\epsilon_{N^+,j}$	$\frac{\epsilon_{N^+,j}}{k}$	$\epsilon_{O^+,j}$	$\frac{\epsilon_{O^+,j}}{k}$	$\epsilon_{O_2,j}$	$\frac{\epsilon_{O_2,j}}{k}$	$\epsilon_{N_2,j}$	$\frac{\epsilon_{N_2,j}}{k}$	$\epsilon_{e,j}$	$\frac{\epsilon_{e,j}}{k}$
1	4	0	5	0	1	0	4	0	3	0	1	0	2	0
2	10	27657	3	228.0	3	70.6	10	38578	2	11390				
3	6	41485	1	325.8	5	188.9	6	58211	1	18990				
4	12	119858	5	22825	5	22031	12	172529						
5	6	123962	1	48609	1	47019	10	238772						
6	12	126793	5	106112	5	67849								
7	2	134614	3	110166	15	132694								
8	20	136395	19	126051	9	157109								
9	12	137374	8	137878										
10	14	139245	84	142875										
11	6	140664												
12	10	143359												
13	18	149498												
14	34	150566												
15	26	150859												
16	30	151129												
17	48	153821												

TABLE II.- RATE CONSTANTS

(a) Chemical Nonequilibrium Rate Constants

Reaction equation number, i	Catalytic body, l	Forward rate constant, ¹ $k_{f,i}$	Efficiency factor, δ_i^l
1	N ₂	$3.0 \times 10^{21} T^{-3/2} \exp\left(\frac{-113260}{T}\right)$	1
	O		1/3
	O ₂		1/3
	N		5
2	O ₂	$3.6 \times 10^{21} T^{-3/2} \exp\left(\frac{-59380}{T}\right)$	1
	O		$0.59 \times 10^{-3} T$
	N ₂		1/3
	N		1/3
3		$5.18 \times 10^{21} T^{-3/2} \exp\left(\frac{-75490}{T}\right)$	
4		$1.0 \times 10^{12} T^{1/2} \exp\left(\frac{-3120}{T}\right)$	
5		$4.5 \times 10^{13} \exp\left(\frac{-38016}{T}\right)$	

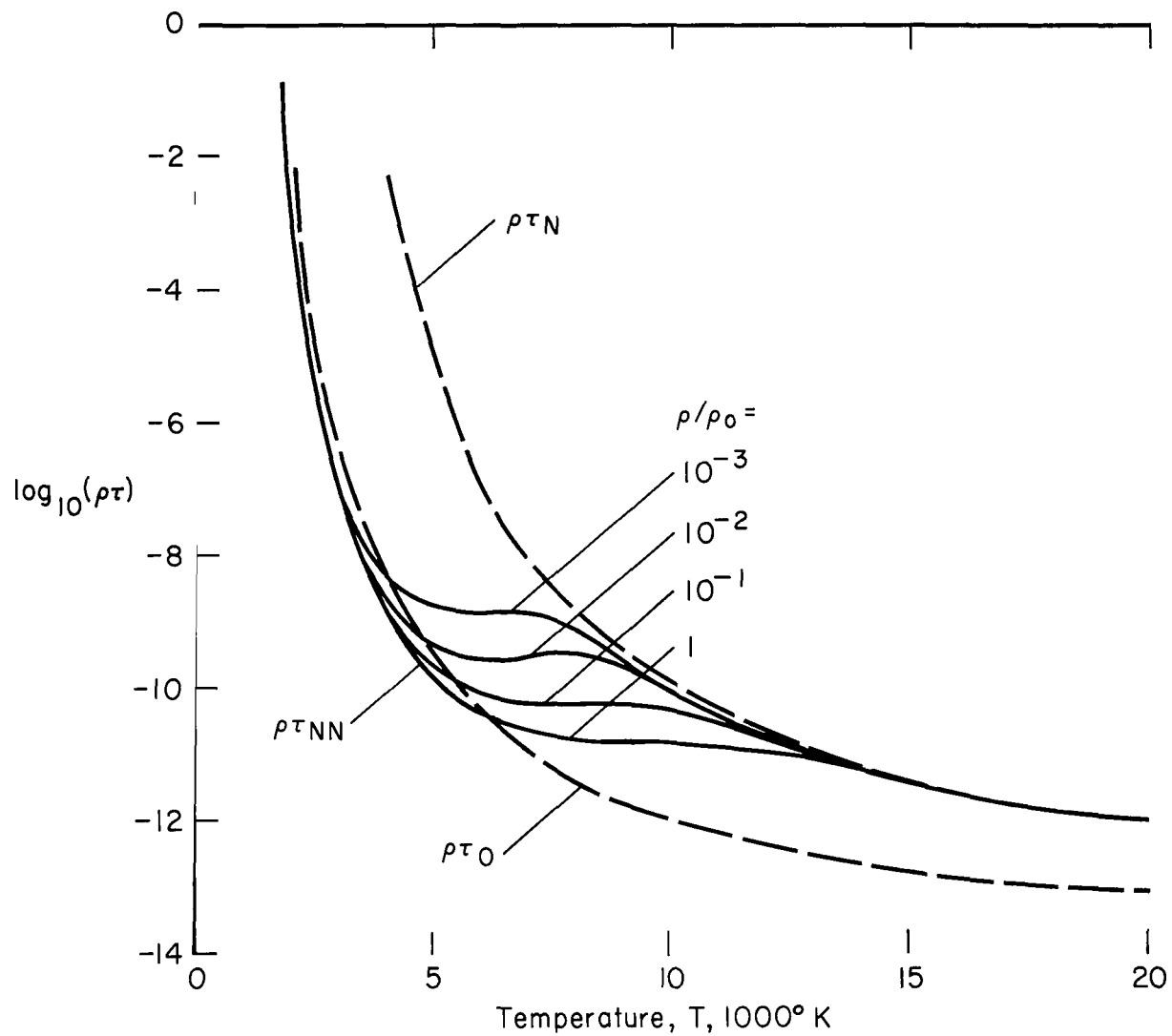
¹Depending on reaction, $k_{f,i}$ has dimensions of cm⁶/mole²-sec or cm³/mole-sec.

(b) Vibrational Nonequilibrium Rate Constants

$$p\tau_{V_{O_2}} = 1.6188 \times 10^{-3} \exp(101.44/T^{1/3}) \text{ dynes-sec/cm}^2$$

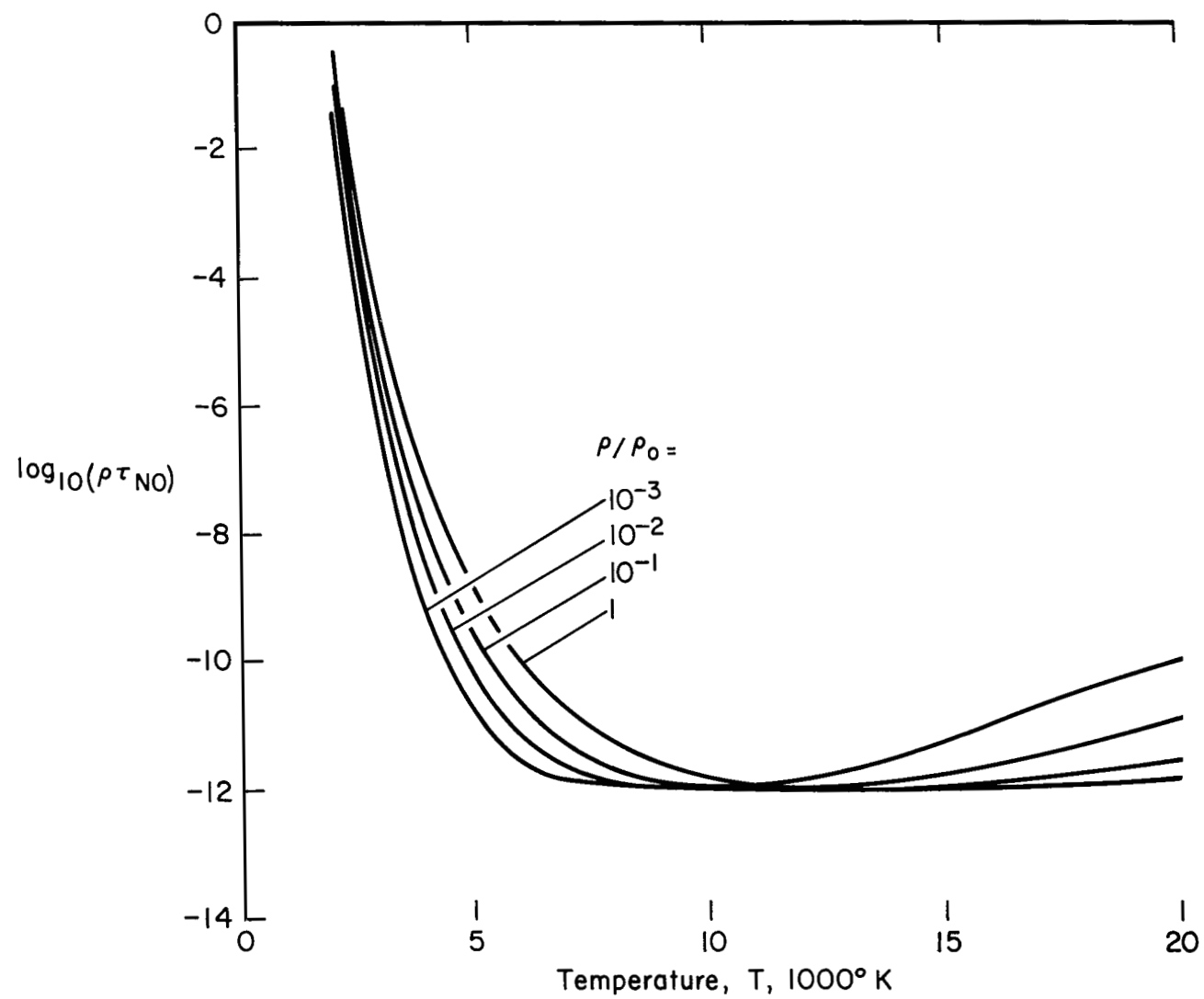
$$p\tau_{V_{N_2}} = 1.11531 \times 10^{-5} \sqrt{T} \exp(154.0/T^{1/3}) \text{ dynes-sec/cm}^2$$

where p is the local value (or static) pressure



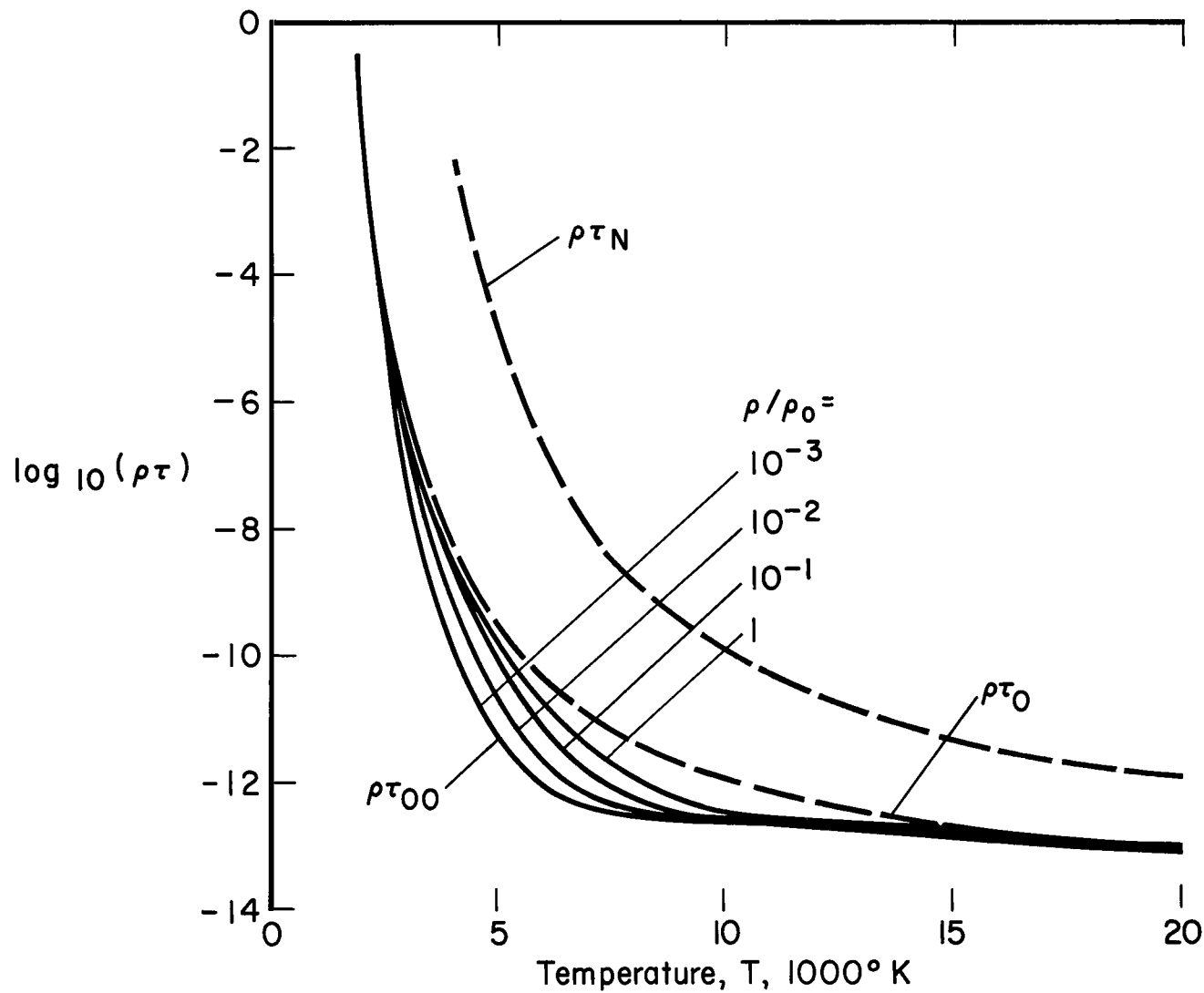
(a) $\rho\tau_{NN}$, $\rho\tau_O$, $\rho\tau_N$ versus temperature.

Figure 1.- Product of density and the characteristic relaxation times that occur in the rate equation for nitrogen.



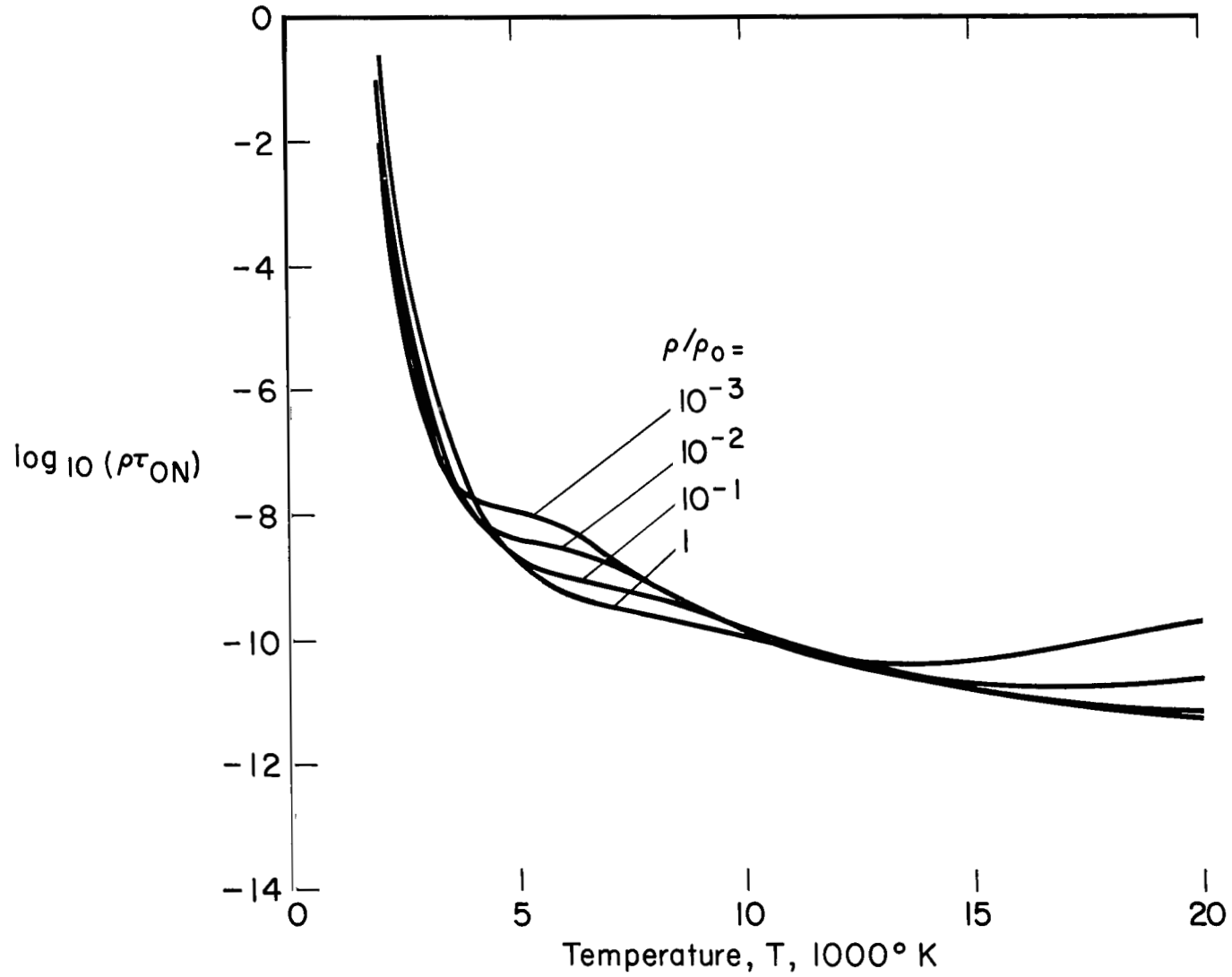
(b) $\rho\tau_{NO}$ versus temperature.

Figure 1.- Concluded.



(a) $\rho\tau_{00}$, $\rho\tau_0$, $\rho\tau_N$ versus temperature.

Figure 2.- Product of density and the characteristic relaxation times that occur in the rate equation for oxygen.



(b) $\rho\tau_{ON}$ versus temperature.

Figure 2.- Concluded.

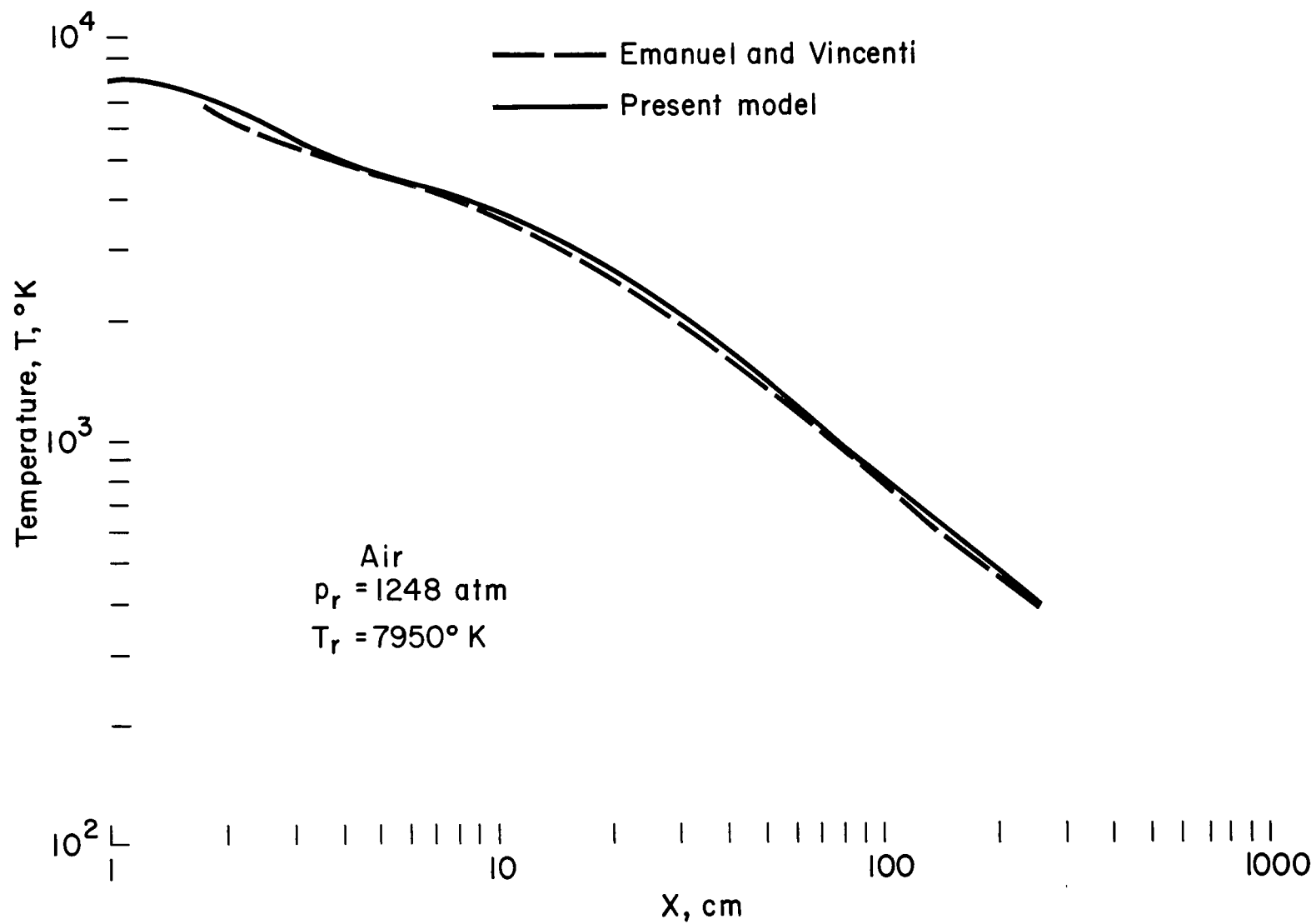


Figure 3.- Comparison of the temperature profile from a nozzle flow calculation by Emanuel and Vincenti (ref. 9) with the profile obtained from the present air model.

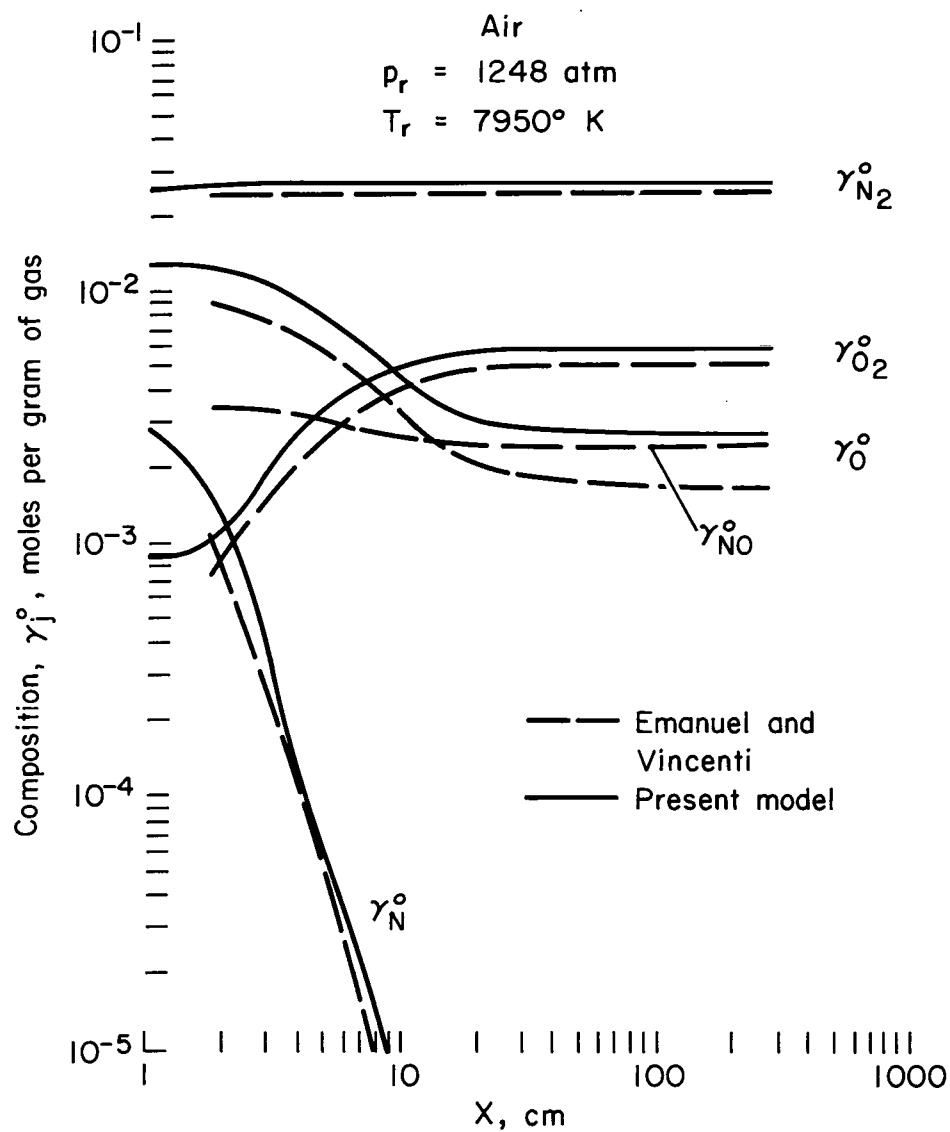


Figure 4.- Comparison of composition profiles in a nozzle according to Emanuel and Vincenti (ref. 9) with those obtained from the present model.

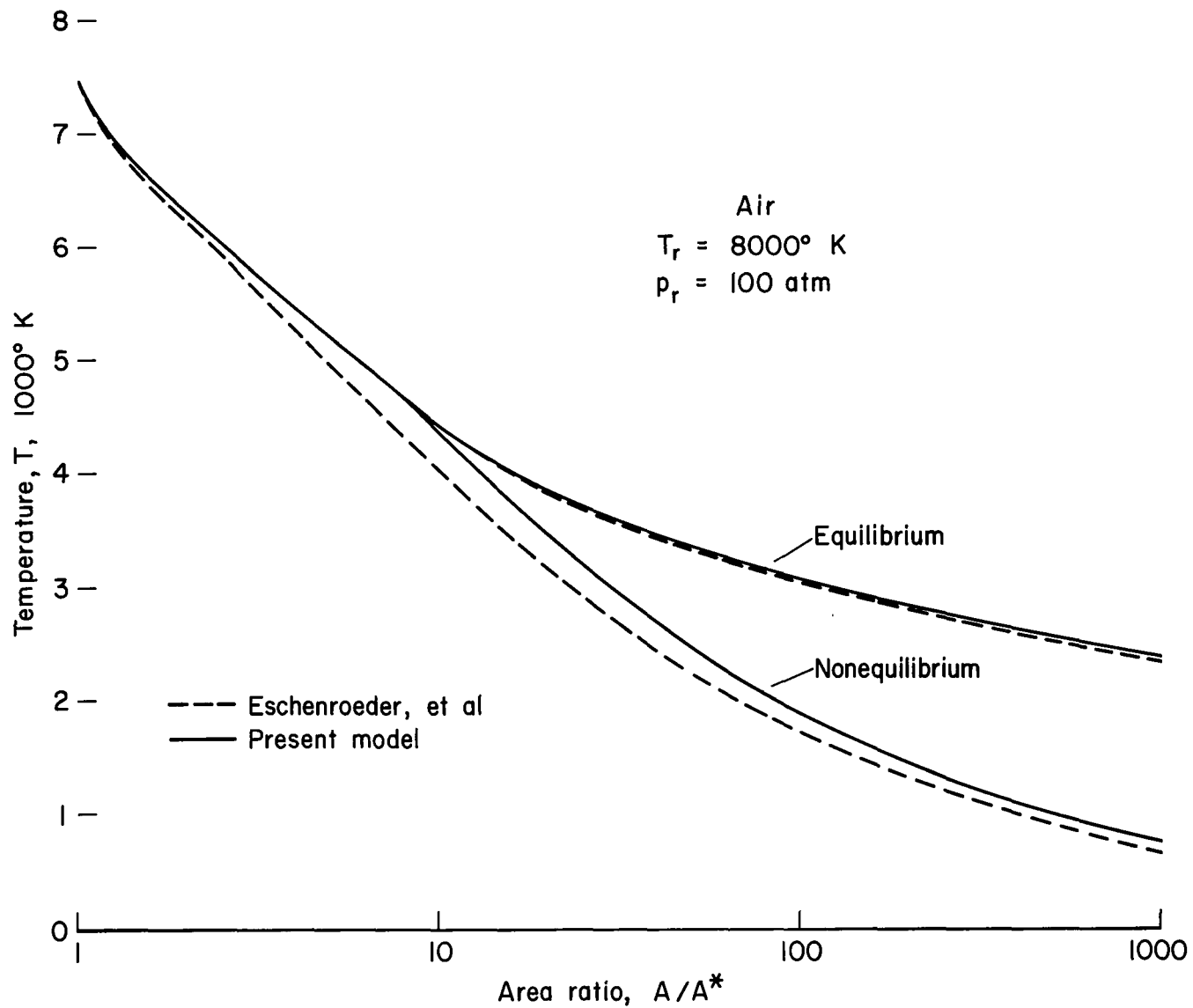


Figure 5.- Comparison of equilibrium and nonequilibrium nozzle temperature profiles obtained from Eschenroeder et al., with those of the model.

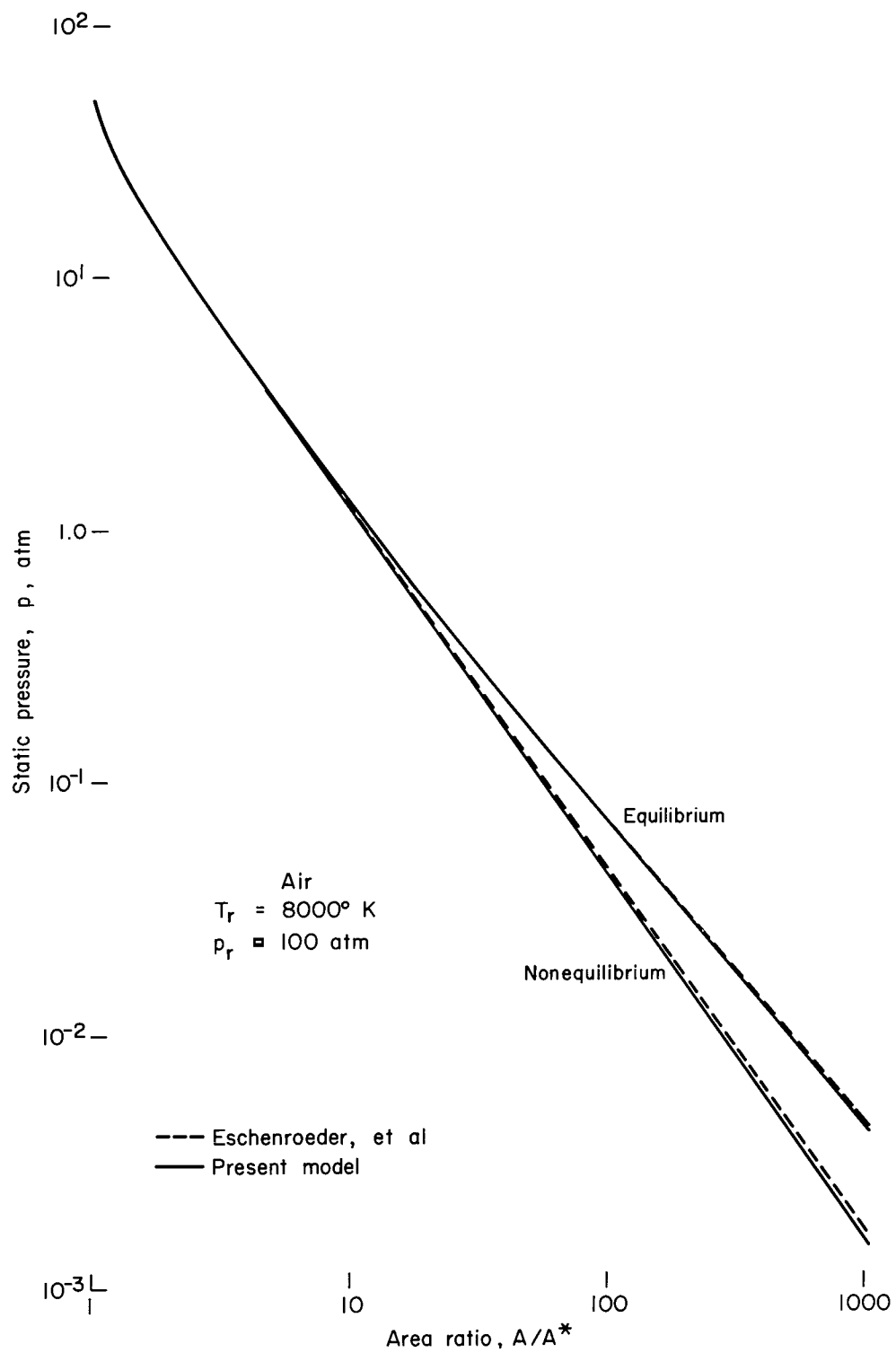


Figure 6.- Comparison of equilibrium and nonequilibrium nozzle pressure profiles obtained from Eschenroeder et al., and the model.

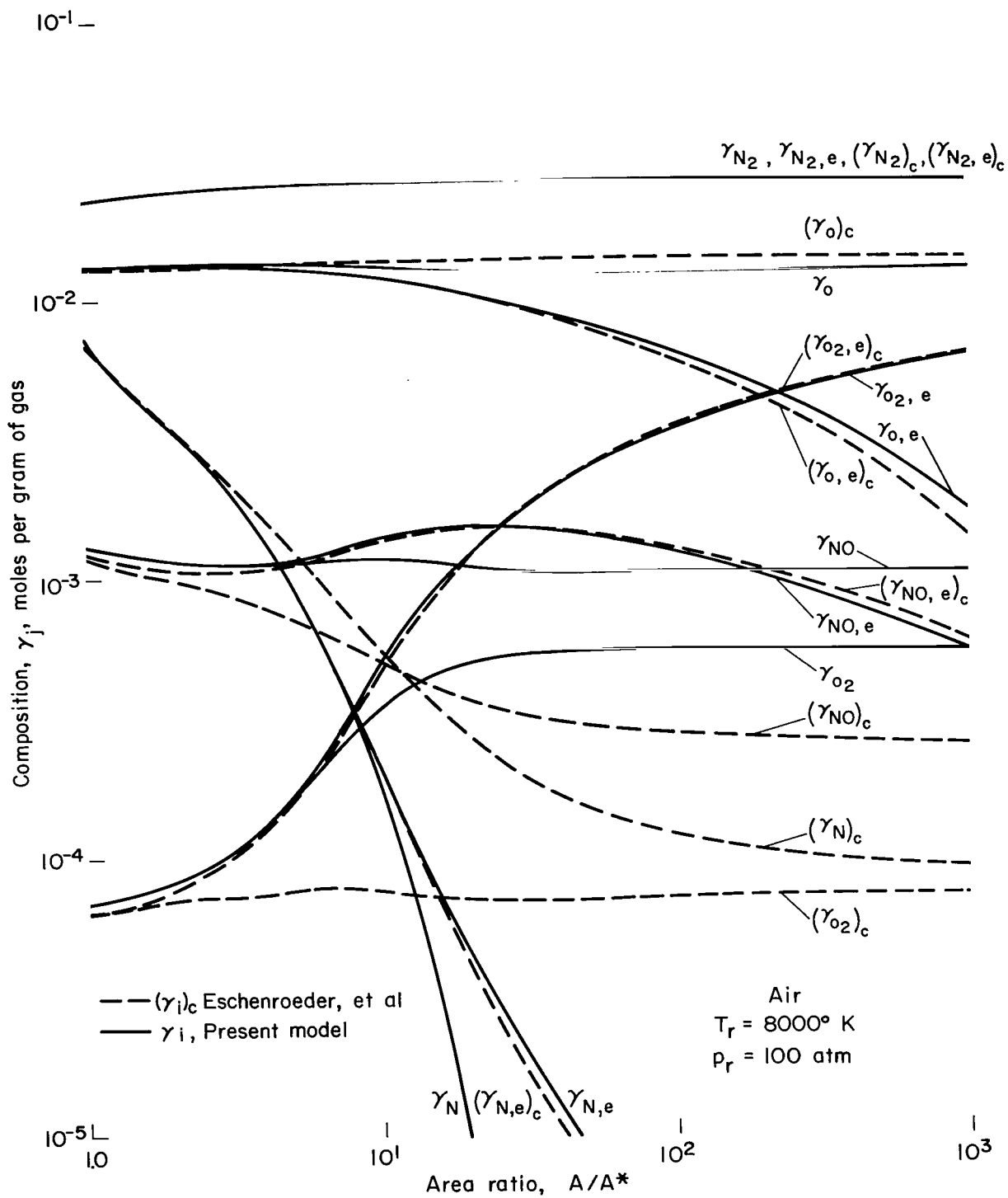
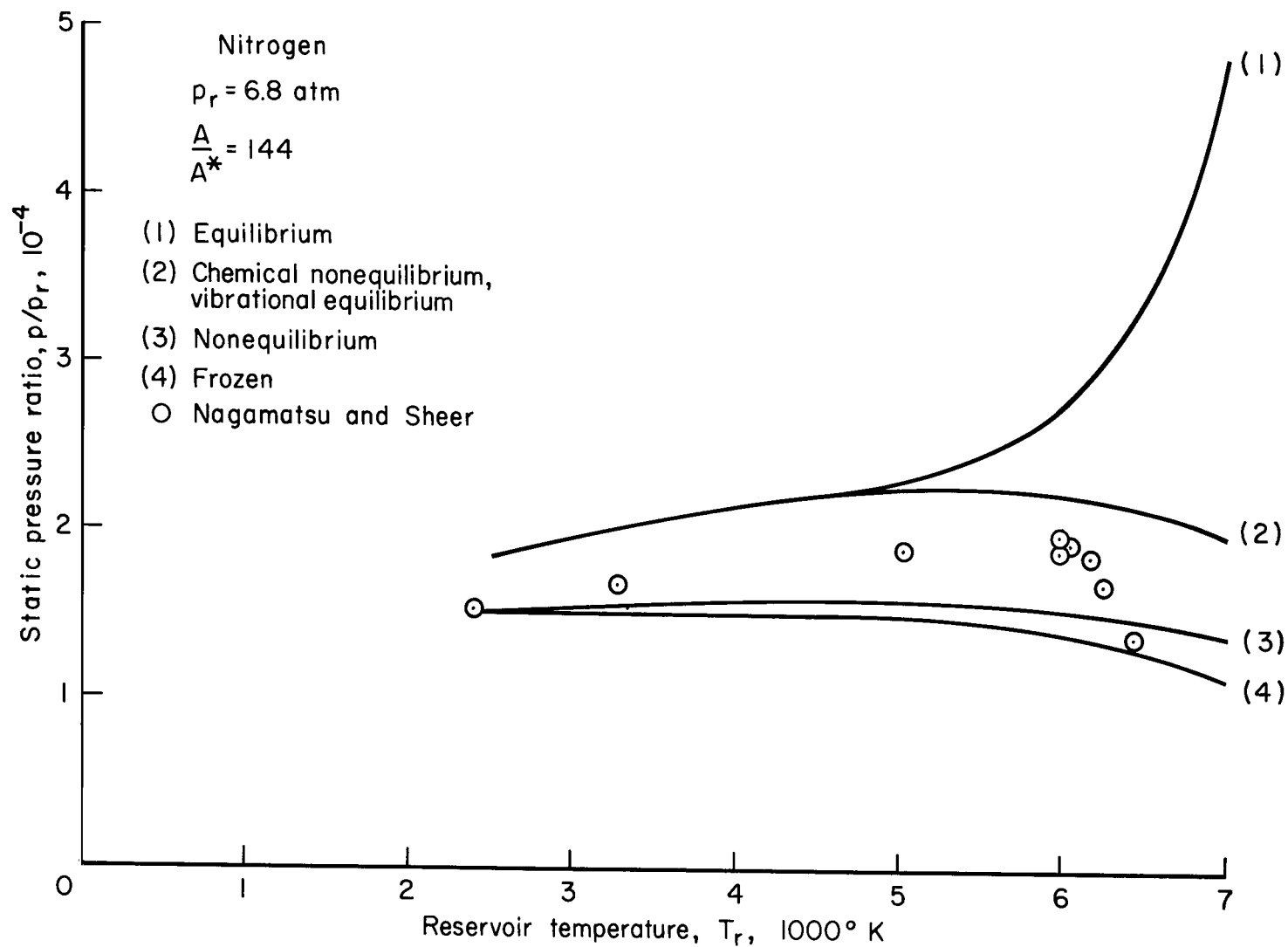
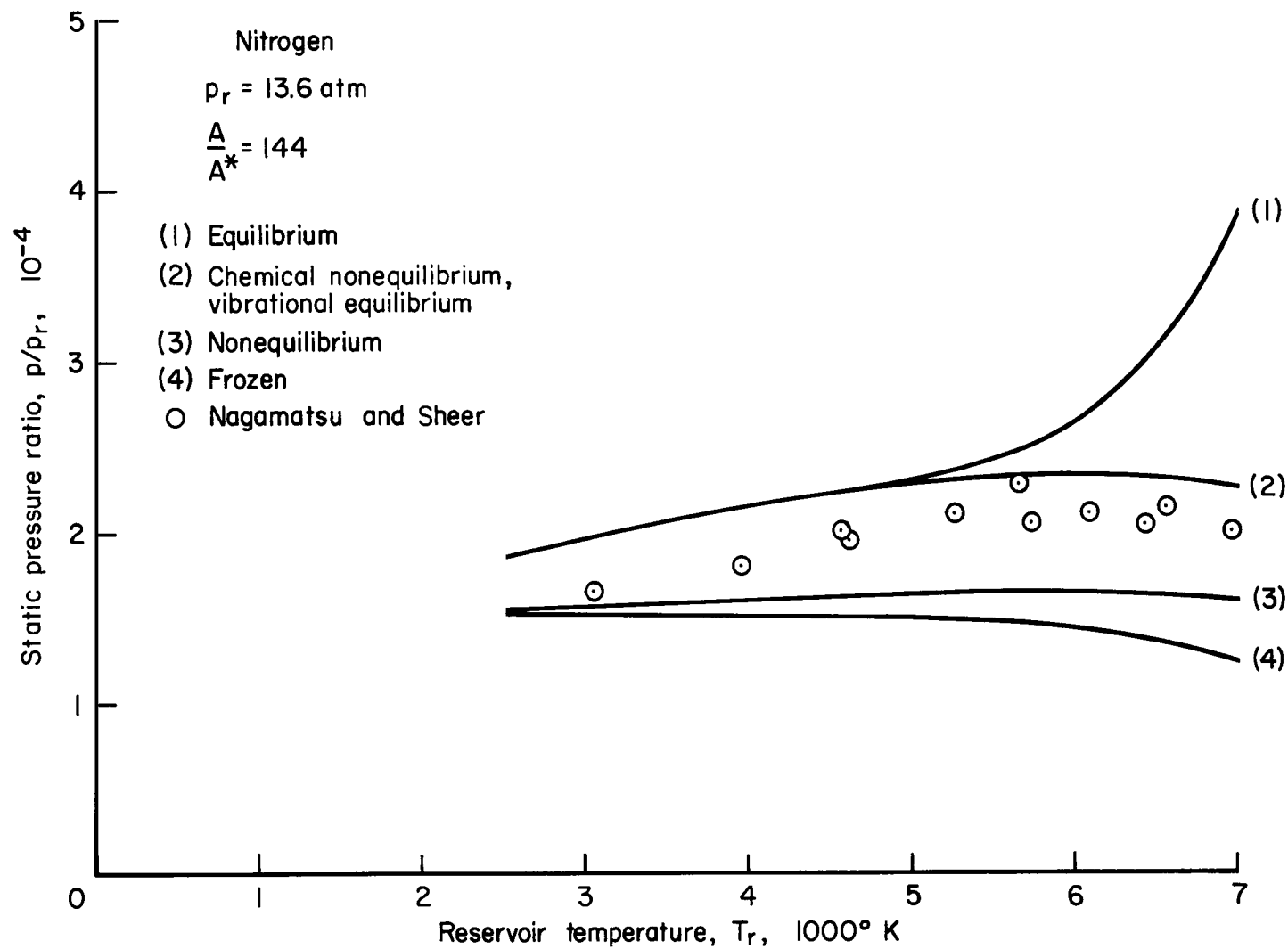


Figure 7.- Comparison of equilibrium and nonequilibrium composition profiles of reference 11 with a corrected form of the model results.



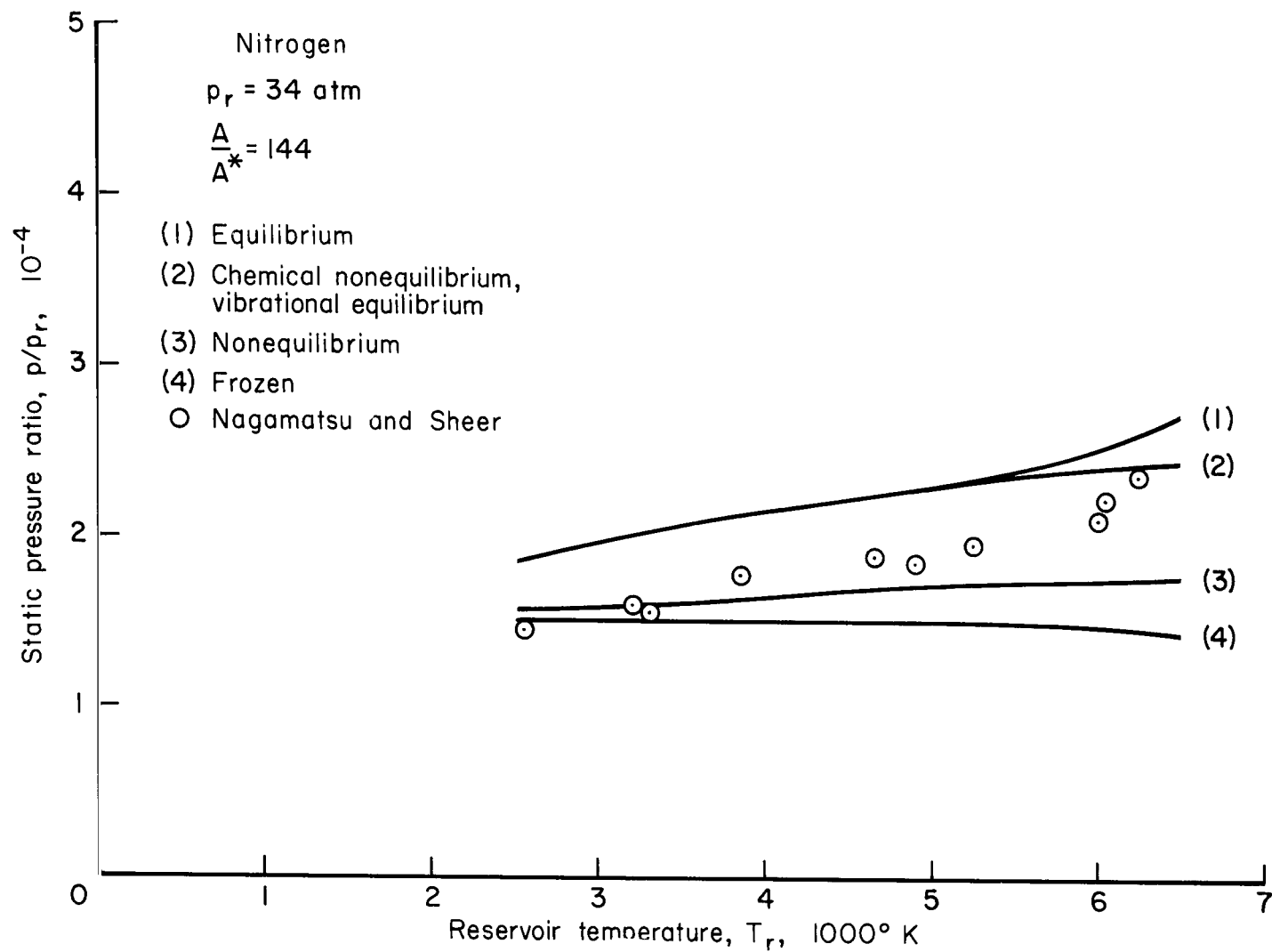
(a) Reservoir pressure equal to 6.8 atm (100 psia).

Figure 8.- Comparison of experimental results for pure nitrogen obtained from Nagamatsu and Sheer (ref. 33) and from a calculation using the integration techniques of this report.



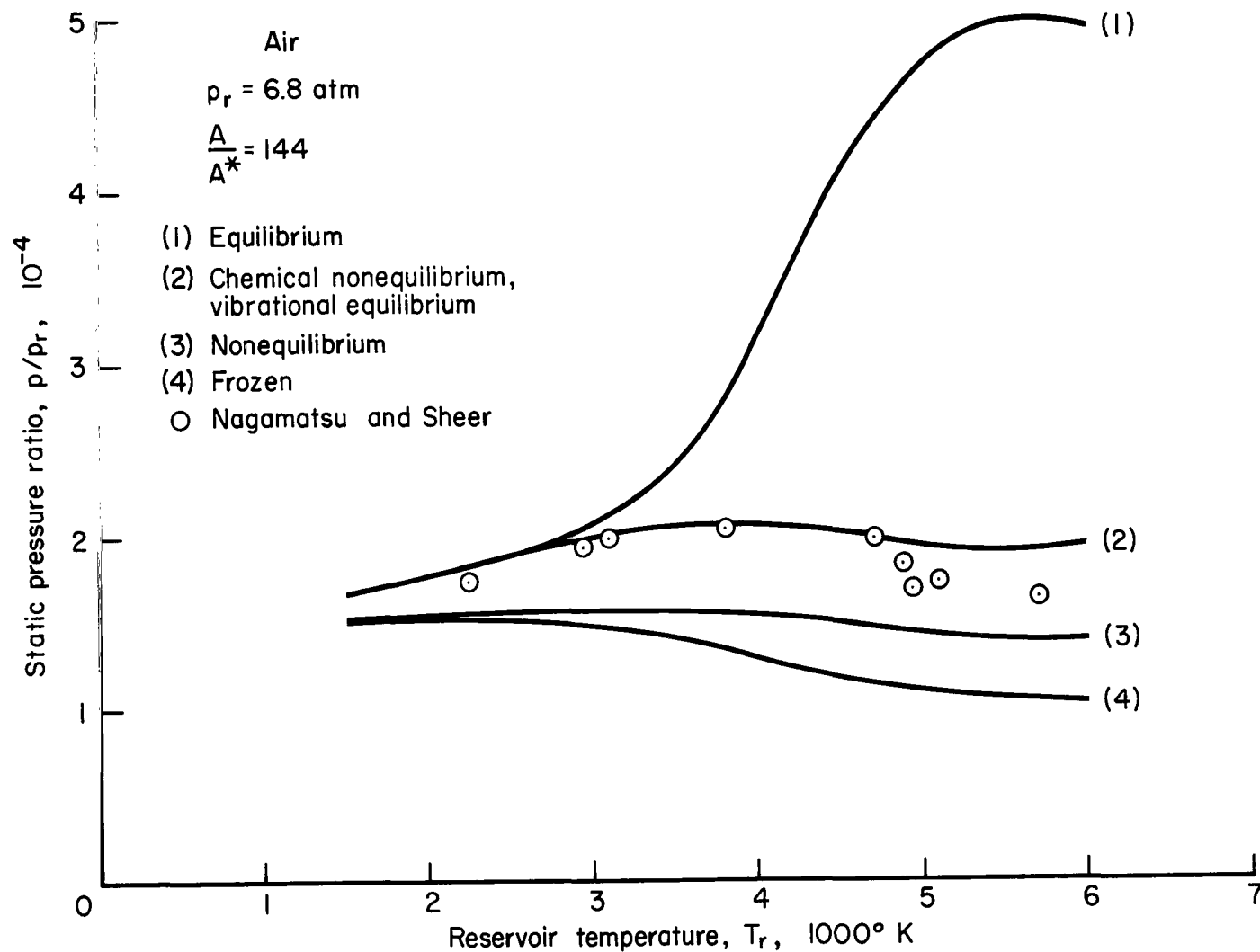
(b) Reservoir pressure equal to 13.6 atm (200 psia).

Figure 8.- Continued.



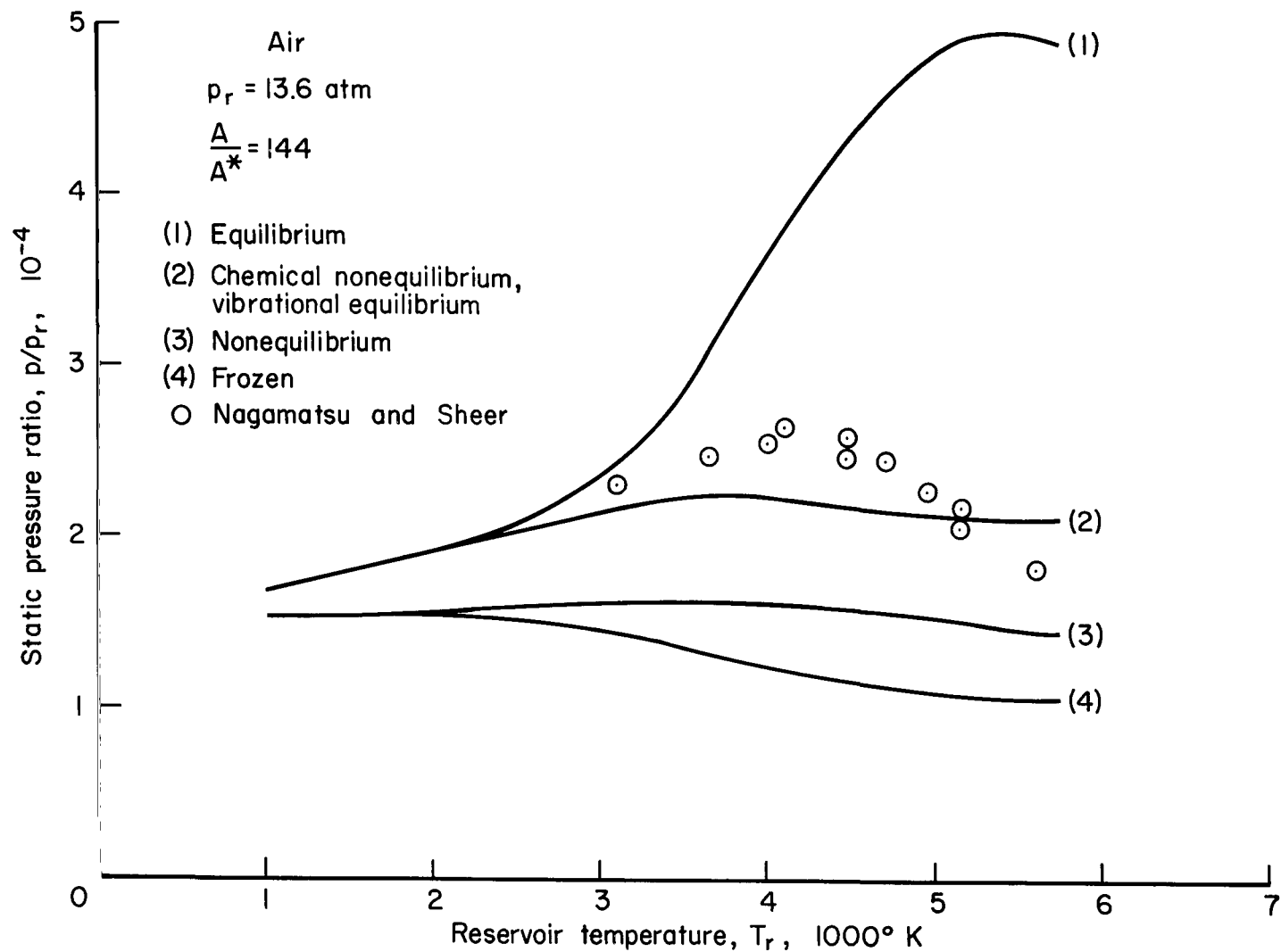
(c) Reservoir pressure equal to 34 atom (500 psia).

Figure 8.- Concluded.



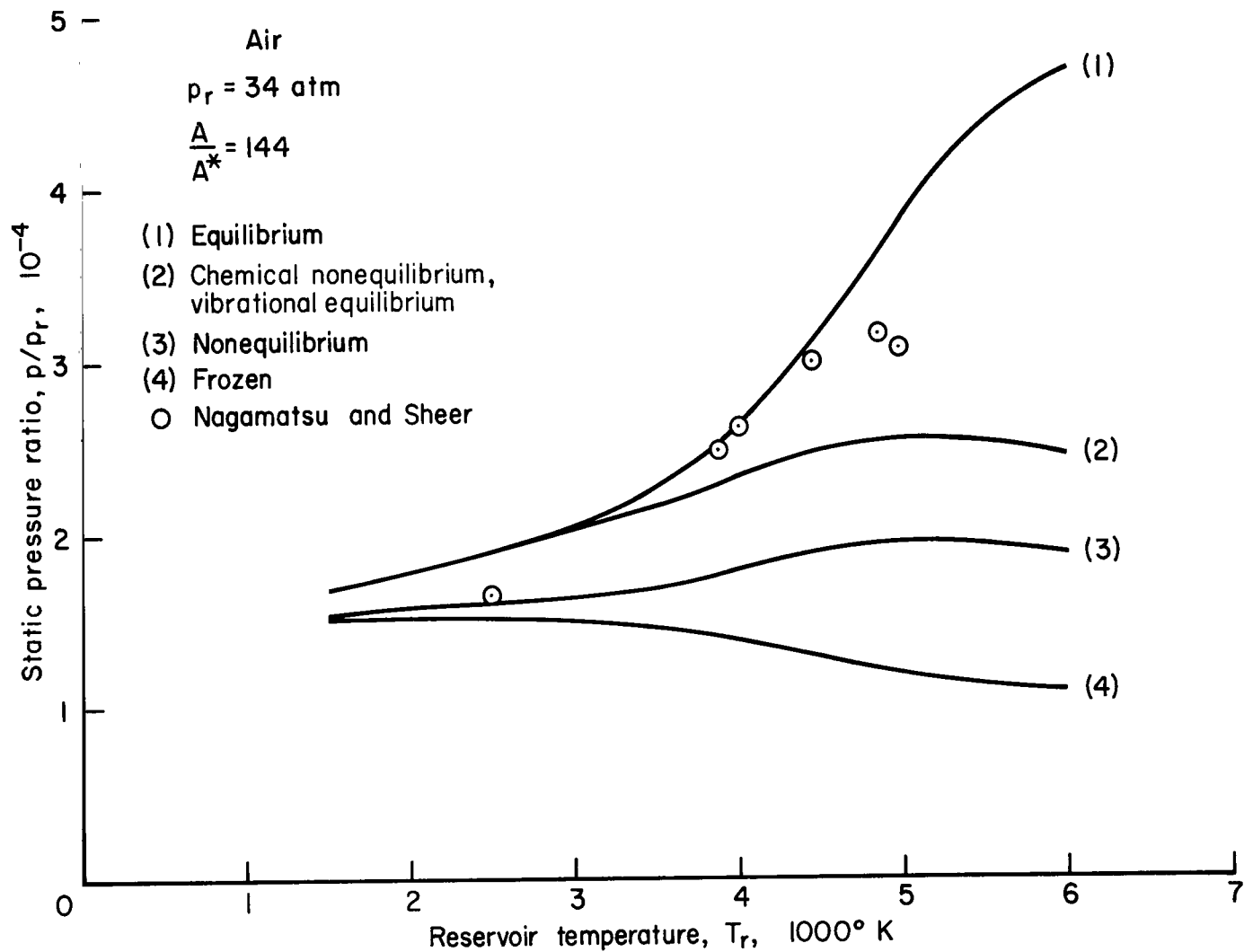
(a) Reservoir pressure equal to 6.8 atm (100 psia).

Figure 9.- Comparison of experimental results for air obtained from Nagamatsu and Sheer (ref. 33) with the air model.



(b) Reservoir pressure equal to 13.6 atm (200 psia).

Figure 9.- Continued.



(c) Reservoir pressure equal to 34 atm (500 psia).

Figure 9.- Concluded.

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"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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